SUMMARY

The object of this research was to study the mass transfer of liquids in porous media at 25°C. The main experimental variables were the initial solute concentration, the method or direction of sorption, the radius of the porous cylinders used, the properties of the porous medium, and the external flow conditions.

Two experimental methods of determining D, the mutual diffusivity, were used to study the system potassium chloride-water.

Previously impregnated alumina-silicate and Teflon porous cylinders were immersed in a large volume of liquid and absorption or desorption allowed to proceed. The mass transfer was measured by two methods:

(1) continuous measurement of the apparent weight of the porous cylinder and contents by a recording balance

(2) continuous measurement of the concentration of solute in the large volume of liquid.

A capacitance cell was used to determine the concentration of solute in the large volume of liquid.

The experimental results indicated very close agreement between the experimental methods.

Work with the recording balance was carried out with potassium chloride-water, sucrose-water and carbon tetrachloride-methanol and the porous media H125, V5, CC2 (all grades of alumina-silicates) and porous Teflon.

The range of concentrations investigated was:- potassium chloride 1N - 3N; sucrose 15 - 30 weight %; carbon tetrachloride 40 - 60 weight %. The range of cylinder radius investigated was:- 0.77 cm. - 0.52 cm.

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Since the plots of apparent weight of cylinder vs the square root of time were substantially linear, the results indicated that the mass transfer was approximately in accordance with Fick's law.

The percentage experimental error was 0.8 - 1.4%. The consistency of the results was slightly better for the results obtained using H125 cylinders than for the results using either V5 or CC2 cylinders. The consistency of the results using Teflon cylinders was bad. This is in accordance with the results of the pore size distribution tests which indicated that the porous media in order of decreasing consistency or reproducibility are H125, CC2, V5, Teflon.

Absorption occurs more quickly than desorption for the aqueous solutions studied but desorption occurs more quickly than absorption for carbon tetrachloride in methanol.

The concentration dependence of the diffusivity appears to be substantially the same, for diffusion in a porous medium and in free solution. The diffusivity was observed to vary slightly with the radius of the porous cylinder for the V5 and CC2 grades of the alumina-silicate porous media. The diffusivity did not depend on the external flow conditions for values of Reynold's Number in the range 100 - 7000.

Although the experimental data is not sufficient to allow accurate postulation of an algebraic relationship, it appears that D decreases linearly as the diameter of the diffusing particle increases.

Two main observations can be made regarding the effect of the porous media: The larger particles are hindered less than the smaller particles by the porous media, i.e. sucrose is hindered less than potassium chloride; the physical property of the porous media which has the greatest effect on the diffusivity is the

porosity or total available pore volume. Experiments with H125 cylinders indicate that the value of D is almost linearly proportional to the porosity. There is no experimental evidence that the ratio of the linear dimensions of the diffusing particle and the pore influences the rate of mass transfer.

A STUDY OF MASS TRANSFER OF LIQUIDS IN POROUS MEDIA

A THESIS SUBMITTED TO GLASGOW UNIVERSITY IN FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

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A C K N O W L E D G M E N T S

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S U M M A R Y

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C O N T E N T S

I L L U S T R A T I O N S

INTRODUCTION

When diffusion in a porous solid determines the rate of a chemical or physical process, a knowledge of the rate of diffusion of the fluid concerned and the factors which influence it are essential for a complete understanding of the process.

The main industrial examples of such processes are

(i) sorption operations such as leaching of porous solids or adsorption of a component of a liquid mixture as a purification step; and

(ii) catalysis of chemical reactions.

Akselrud (1) has suggested a method for determining the pore distribution function for volumes of ideal pores from simple experimental extraction data similar to this author's data and has shown how the distribution function can be applied to practical problems such as co-current and countercurrent extraction.

Thiele (2) stated that the size of catalyst grains could not be increased indefinitely without ultimately reaching a point at which the reaction would produce products in the grain interior faster than diffusion could carry them away. Representing the porous structure by a simplified model and assuming a first order chemical reaction, he showed that the ratio of the reaction rate with a given grain size to the rate if the composition of fluid throughout the grain were the same as in the fluid surrounding the grain depended on a dimensionless modulus, in which the effective diffusion coefficient was included.

Aris (3) and Carberry (4) extended Thiele's ideas and showed that his relationship was valid for any shape of grain.

Thus there are practical reasons for determining the effective diffusion coefficient of a liquid in a porous solid. The scope of the work attempted is given in the next section.

1.1 Object of the Research

The object of the research was to investigate the factors which influenced the isothermal mass transfer of liquids in porous media. The factors studied were:-

The solute-solvent system, the properties of the porous media, the direction of mass transfer, and the flow regime.

These four factors are now considered individually.

Solute-Solvent System

The most important classification was the system type - organic or inorganic. Two inorganic systems and one organic system were studied. For the inorganic systems, in which water was the solvent, two solutes were studied, an electrolyte and a non-electrolyte. In each case the effects of solute concentration, diameter of the diffusing particle, and mutual diffusivity in free solution were investigated.

Properties of the Porous Media

The physical characteristics of the porous media which were investigated were the geometry of the porous sample, the percentage porosity, the tortuosity of the pore system, and the pore size distribution.

Direction of Mass Transfer

Absorption and desorption experiments were carried out to try to verify the theoretical prediction of Crank and Henry (5). This stated that where the diffusivity in free solution increases with increasing solute concentration, the process of absorption should take place more quickly than desorption and conversely where the diffusivity in free solution decreases with increasing solute concentration the process of desorption should take place more quickly than absorption.

Flow Regime

Experiments were carried out at various flow conditions to ascertain the magnitude of the resistance to mass transfer at the solid-liquid interface.

It was hoped that the effective diffusivity of a solute-solvent system in a porous solid could be predicted from a knowledge of the physical properties of the solute-solvent system and the solid. For this reason the main correlations for predicting the diffusivity in free solution are given below.

1.2 Summary of Research on the Diffusivities of Liquids in Free Solution

Since the beginning of the twentieth century, much attention has been focused on the problem of predicting diffusivities of liquids from a knowledge of their physical properties. The attempts to correlate diffusivities and fundamental physical properties can be classified as:-

(1) The theoretical approach.
(2) The semi-empirical approach, and
(3) The empirical approach.

1.2.1. Theoretical Approach

Several attempts have been made to describe transport processes and to predict the coefficients of diffusion and viscosity. The first attempt was an adaptation of the kinetic theory of liquids.

1.2.1(a) Kinetic Theory of Liquids

Arnold (6), assuming the rate of momentum transfer to be the product of the number of binary collisions per second, equated this rate to the force causing diffusion and he derived, for ideal solutions,

$$D_{12} = \frac{B \left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{\frac{1}{2}} \cdot V_2}{S^2} \qquad \text{.....(1)}$$

where D_{12} = mutual diffusivity of species 1 in species 2.
M_1, M_2 = molecular weights of species 1 and 2 respectively.
V_2 = molar volume of species 2 (solvent).
S^2 = square of the sum of the molecular diameters.

In the derivation of equation (1), three assumptions were made:-

(1) All collisions are binary, involving two molecules only.
(2) The collision rate is unaffected by the volume occupied by the molecules.
(3) The intermolecular attractions do not come into play.

None of these assumptions is valid for liquids. Arnold took account of the failure of the three assumptions by means of a semi-empirical factor F which was inserted in the denominator of equation (1). By empirical examination of data on the diffusion of dilute non-electrolytes, Arnold determined the value of F. The complete expression for F is:-

$$F = A_1 A_2 V_2 Z_2^{\frac{1}{2}}$$

where A_1, A_2 = factors to take into account the degree of association of the solute and solvent respectively.

Z_2 = viscosity of the solvent.

Thus, for real solutions, the expression for the mutual diffusivity became

$$D_{12} = \frac{B \left(\frac{1}{M_1} + \frac{1}{M_2}\right)^{\frac{1}{2}}}{A_1 A_2 Z_2^{\frac{1}{2}} S^2} \qquad \text{.....(2)}$$

Since equation (2) contains three adjustable parameters, A_1, A_2, B, it is not surprising that experimental results agree with it and it cannot truly be called a theoretical but rather a semi-empirical correlation.

The derivation of equations (1) and (2) depends on the assumption that the gaseous and liquid states are similar. Consideration of such physical properties as latent heats of evaporation and fusion, volume changes during evaporation and fusion, and specific heats of solids, liquids and gases led Frenkel (7) to suggest that the liquid state bore much more resemblance to the solid state than to the gaseous state. This would explain the discrepancies between experimental diffusivities and those predicted by equations (1) and (2).

1.2.1 (b) Viscosity-Diffusivity Relationship

Einstein (8) and Sutherland (9) proposed that the balance between a driving force of the gradient of chemical potential and a resistance to flow leads to a constant average diffusion velocity. They derived the expression:-

$$D_{12} = \frac{RT\, B_2^{c}}{N\, W} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

where D_{12} = mutual diffusion coefficient in a 2 component system.

R = gas constant.

T = absolute temperature.

N = Avogadro Number.

W = viscous resistance per molecule.

$B_2^{c} = \left[\, 1 + \left(\frac{\partial \ln f_2}{\partial \ln N_2}\right)_{T,\,P}\right]$ for component 2;

the activity correction for non-ideality.

Stokes showed that:

$$W = 6\pi\, \eta_1\, r_2\, \frac{1 + \beta\, r_2}{1 + \frac{3\eta_1}{\beta\, r_2}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

where β = the coefficient of sliding friction between the diffusing molecule and its surroundings.

η_1 = viscosity of component 1 (solvent).

r_2 = radius of diffusing molecule.

The two limiting values of β are:

$$\beta = 0 \qquad W = 4\pi \eta_1 r_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

$$\beta = \infty \qquad W = 6\pi \eta_1 r_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Sutherland stated that for a large spherical molecule in a medium of low molecular weight, little "hydrodynamic slip" would occur and (7) would apply.

Thus $$D_{12} = \frac{RT}{6\pi \eta_1 N r_2}$$ for an ideal solution ....(8)

Sutherland also stated that for a small molecule diffusing through a medium of comparable molecular weight, $\beta = 0$ and

$$D_{12} = \frac{RT}{4\pi \eta_1 N r_2}$$ for an ideal solution .....(9)

Experimental data gave reasonable agreement with equation (8) for large solute molecules in a medium of much smaller molecules (10).

Neither of these theories gave a completely satisfactory method of predicting diffusion coefficients.

The modern approach is more radical and is based on a generalised picture of the liquid state which can be mathematically treated using the methods of statistical mechanics and the thermodynamics of irreversible processes.

1.2.1 (c) Statistical Mechanical Interpretation

Before proceeding with the application of statistical mechanics to diffusion problems, the meaning of the distribution function will be given. The distribution function describes the

probability of one molecular arrangement and a knowledge of the variation of the distribution function with time leads to an understanding of transport phenomena. Diffusion is treated as a process controlled by random walk with very small steps.

Statistical Mechanics Applied to Binary Liquid Diffusion

Kamal and Canjar (11) claim a correlation, based on statistical mechanics, which agrees with 56 different solute-solvent systems to 13% deviation. Their argument will be summarised below.

Kirkwood's theory of transport phenomena in dense media (12) was developed by Rice to give:

$$D = \frac{k\,T}{W} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

where D = self diffusivity.

Further derivation yielded

$$D = \frac{5\,k\,T\,V_o\,\eta_v}{m} \left[\frac{1}{24L - 15\,pV_o - 15\,RT}\right] \quad \ldots \quad (11)$$

where V_o = molar volume.

η_v = interaction energy contribution to shear viscosity.

m = mass of a molecule.

L = internal energy of vaporisation $\simeq (\Delta H_{vap.} - RT)$

and finally

$$D = 1.2021 \times 10^{-8} \left(\frac{RT}{\pi M}\right)^{\frac{1}{2}} \frac{V_o^{1/3}}{(v_o/v)^{2/3}} \left[1.6\,\frac{v_o}{v} + 2.56\,\frac{v_o}{v}^2\,g^2\,(\sigma)\right] . \quad (12)$$

$$\times \left[\frac{RT}{24L - 15\,pV_o - 15\,RT}\right]$$

where $g^{(2)}(\sigma) = 1 + 2.5\,\frac{v_o}{v} + 4.5864\left(\frac{v_o}{v}\right)^2 \qquad \ldots\ldots\ldots\ldots \quad (13)$

v = total volume per molecule.

v_o = occupied volume per molecule

$\left(\frac{v_o}{v}\right)$ was found from the equation of Collins and Navidi based on the velocity of sound at low frequencies.

From equation (11) the self diffusivity can be split into two parts, viz - $\frac{5\ k\ T\ V_o\ \eta v}{m}$ which represents the driving force and the net resistance inherent in the diffusion medium which leads to Brownian motion of that medium; and $\frac{1}{24L - 15\ p\ V_o - 15\ RT}$ which represents the resistance due to the nature of the diffusing solute and interactions with solvent molecules.

Mutual Diffusion

In a binary solution the net resistance to Brownian motion is due to interactions of the solute molecules with each other and with molecules of the solvent. At infinite dilution it can be assumed that Brownian motion of the solvent is not affected by solute molecules. So the first term for self diffusivity is also valid for mutual diffusivity at infinite dilution. The internal energy (L) is estimated to be the heat of vaporisation of the solute and it is assumed that after this energy is overcome, the solute molecule is under the influence of the Brownian motion of the solvent. Thus D_{12}^{∞}, the mutual diffusivity at infinite dilution is:

$$D_{12}^{\infty} = 1.2021 \times 10^{-8} \left[\left(\frac{RT}{\pi M}\right)^{\frac{1}{2}} \frac{V_o^{1/3}}{(V_o/v)^{2/3}} \left\{1.6\ \frac{v_o}{v} + 2.56\left(\frac{v_o}{v}\right)^2 N.\ g^{(2)}\ (\sigma)\right\}\right]_{solvent} \times \left[\frac{RT}{24L - 15\ pv - 15\ RT}\right]_{solute} \quad \ldots\ (14)$$

Kamal and Conjar (11), using Darken's equation (13) obtained for the variation of mutual diffusivity with concentration:-

$$D_{12} = [N_1\ D^{*}_{2} + N_2\ D^{*}_{1}] \left[1 + N_2 \frac{\partial \ln \gamma_2}{\partial N_2}\right] \quad \ldots\ (15)$$

where D^{*}_{i} = diffusivity of an isotope tracer of i in the solution.

N_i = mole fraction of component i in the solution.

γ_1 = activity of component i in the solution.

Equation (14) can be rewritten:

$$D_{12}^{\infty} = B\, f(\Delta H) \quad \ldots\ldots (16)$$

where $$B = 1.2021 \times 10^{-8} \left(\frac{RT}{\pi M}\right)^{\frac{1}{2}} V_o^{1/3} A \quad \ldots\ldots (17)$$

$$A = \left[1.6\,\frac{v_o}{v} + 2.56\left(\frac{v_o}{v}\right)^2 N g^{(2)}(\sigma)\right]\left(\frac{v_o}{v}\right)^{-2/3} \quad \ldots\ldots (18)$$

$$f(\Delta H) = \frac{RT}{24\,\Delta H_{vap.} - 39\,RT} \quad \ldots\ldots (19)$$

A, B and $f(\Delta H)_{vap.}$ were calculated for 56 solute-solvent systems and compared with experimental values.

There was an average deviation of 13% from experimental values of the diffusion coefficient at infinite dilution. Wilke's equation (see section on Empirical Correlations) gave an average deviation of 10%.

For the system, acetic acid - carbon tetrachloride, the temperature coefficient from equation (14) was lower than the experimental whereas Wilke's temperature coefficient was higher than the experimental.

The variables affected by temperature are $T^{\frac{1}{2}}$, $V_1^{1/3}$, ΔH and A. As the temperature increases all the variables increase except A which decreases slowly with temperature. The exception is water where A increases with temperature. Thus this theory explains the high temperature coefficient of diffusivity of systems with water as the solvent.

When comparing the variation of the mutual diffusion coefficient with concentration predicted by equation (15) with experiment there are two cases.

(i) For ideal solutions, the activity factor, $\left(1 + \frac{\partial \ln \gamma_2}{\partial N_2}\right)$ is unity and $D_{12} = N_1 D^{*}_{2} + N_2 D^{*}_{1}$ ..... (20)

Experiments with ideal solutions, e.g. chlorobenzene-bromobenzene, toluene-chlorobenzene, and benzene-carbon tetrachloride yielded graphs linear with mole fraction as predicted by equation (20).

(ii) For non-ideal solutions, the activity factor had to be evaluated. The system ethanol-water agreed very well with equation (15) and the system methanol-water gave fairly good agreement.

Both Bearman (14) and Laity (15) take as their starting point the "frictional force equation".

Bearman gives:

$$F_{\alpha}^{(1,1)\mathfrak{M}} = \frac{1}{2} \sum_{\beta=1}^{\gamma} \int C_{\beta}\left(\frac{\tau}{r}\right) \frac{d\, V_{\alpha\,\beta}}{d\, r} \left(G_{\alpha\,\beta}^{(2,1)} - G_{\beta\,\alpha}^{(2,1)} \right) d^{3}\tau \quad \ldots (21)$$

where $\bar{F}_{\alpha}^{(1,1)\mathfrak{M}}$ = mean frictional force acting on a molecule of species α in a system containing γ components undergoing one-dimensional, isobaric, isothermal diffusion.

C_{β} = concentration of species β in molecules/unit volume

$V_{\alpha\,\beta}$ = potential of intermolecular force between molecules of α and β, assumed to depend only on the magnitude r of the vector distance τ, which separates the molecules and not on the orientation of the molecules. $G_{\alpha\,\beta}^{(2,1)}$ and $G_{\beta\,\alpha}^{(2,1)}$ are distribution functions.

One of the objectives of the statistical mechanical theory is to determine $G_{\alpha\,\beta}^{(2,1)}$ in terms of $G_{\alpha\,\beta}^{(2,0)}$, the radial distribution function and thus express transport properties in terms of equilibrium functions of state.

Laity's starting point is

$$F = \frac{1}{2} \sum_{i}^{N} \sum_{k} Rik\, (J_i \cdot J_k) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (22)$$

where F = dissipation function for a system of N components at constant temperature and pressure.

J_i, J_k = local fluxes of components i and k respectively.
R i k = friction coefficient.

Both Bearman and Laity state that shortly after a concentration gradient is established in a system, a quasi-stationary state is reached in which the driving force for diffusion, the negative of the chemical potential gradient, becomes sensibly equal in magnitude but opposite in sign to the frictional force.

So Bearman gives:

$$\frac{d\,\mu_\alpha}{dx} = \bar{F}_\alpha(1,1)^\alpha = -\sum_{\beta=1}^{\nu} C_\beta\, W_{\alpha\beta}(u_\alpha - u_\beta) \quad \cdots\cdots\cdots (23)$$

and Laity gives:

$$\nabla\mu_i = -\sum_{k}^{N} Rik\; Ck\; (v_i - v_k) \quad \cdots\cdots\cdots\cdots\cdots\cdots (24)$$

It is obvious that equations (23) and (24) are the same

where $\frac{d\,\mu_\alpha}{dx} = \nabla\mu_1$ = chemical potential gradient.

$W_{\alpha\,\beta}$ = Rik = friction factor.

C_k = C_β = concentration of component k and β respectively.

u_α, u_β, v_i, v_k = local velocity vectors.

So only the Bearman derivation will be continued here, although that of Laity will be referred to below.

For a 2 component system equation (23) reduces to:

$$\frac{d\,\mu_1}{dx} = -C_2\, W_{12}\, (u_1 - u_2). \quad \cdots\cdots\cdots\cdots\cdots\cdots (25)$$

$$\frac{d\,\mu_2}{dx} = -C_1\, W_{12}\, (u_2 - u_1) \quad \cdots\cdots\cdots\cdots\cdots\cdots (25)$$

Using the expressions $j_1^o = C_1\,(u_1 - u_0)$ $\cdots\cdots\cdots\cdots\cdots\cdots (26)$

$$v_1\, j_1^o + v_2\, j_2^o = 0 \cdots\cdots\cdots\cdots\cdots\cdots (27)$$

Where j_1^o = the flux of component i with respect to a volume fixed reference plane.

v_i = the partial molar volume of component i.

Bearman finally arrived at the expressions for mutual diffusion coefficient

$$D = \frac{v_1 \, k \, T}{W_{12}} \left[1 + \left(\frac{\partial \ln f_2}{\partial \ln C_2}\right)_{T, p}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (28)$$

$$= \frac{v_2 \, k \, T}{W_{12}} \left[1 + \left(\frac{\partial \ln f_1}{\partial \ln C_1}\right)_{T, p}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (28)$$

where the activity coefficients f_α are defined by

$$\mu_\alpha = \mu_\alpha^o (T, p) + k \, T \ln a_\alpha$$

$$a_\alpha = f_\alpha \, C_\alpha$$

Regarding the variation of mutual diffusion coefficient with concentration, Bearman showed that when the ratios of friction coefficients (which vary with composition) are constant

$$\frac{D_1}{D_2} = \frac{v_2}{v_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (29)$$

where D_1 and D_2 are the self diffusivities of species 1 and 2 respectively.

Thus, using equation (10) for self diffusivity he derived

$$D = D_1 \left[1 + \left(\frac{\partial \ln f_1}{\partial \ln C_1}\right)_{T, p}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (30)$$

$$= D_1 \left(\frac{\partial \ln a_1}{\partial \ln c_1}\right)_{T, p} \quad \ldots\ldots\ldots\ldots\ldots\ldots (30)$$

and since $\left(\frac{\partial \ln a_1}{\partial \ln c_1}\right)_{T, p} = \left(\frac{\partial \ln a_1}{\partial \ln x_1}\right)_{T, p} \left[\frac{x_1 \, v_1 + x_2 \, v_2}{v_2}\right]$ ..(31)

the final equation is

$$D = \left(\frac{\partial \ln a_1}{\partial \ln x_1}\right)_{T, p} [D_2 \, x_1 + D_1 \, x_2] \quad \ldots\ldots\ldots\ldots (32)$$

Statistical mechanical theory states that when the equilibrium radial distribution functions are independent of composition, i.e. for regular solutions, $D_1\eta$ is independent of composition.

When equation (30) is multiplied by η and $D_1\eta$ is replaced by $D^\infty \eta_2$.

where D^∞ = mutual diffusivity at infinite dilution (i.e. pure 2).

and η_2 = viscosity of pure component 2.

then $$D\eta = D^\infty \eta_2 \left[1 + \left(\frac{\partial \ln f_1}{\partial \ln c_1}\right)_{T,p}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots (33)$$

Similarly, equation (32) becomes

$$D\eta = \left[D^\infty \eta_2 \left(\frac{V_1}{V_2} - 1\right) x_1 + D^\infty \eta_2\right] \left(\frac{\partial \ln a_1}{\partial \ln x_1}\right)_{T,p} \quad \ldots (34)$$

Equations (30), (32), (33) and (34) are all different ways of predicting the dependence on composition of the mutual diffusivity according to statistical mechanical theory.

It is obvious that equations (15) and (32) are identical.

Horrocks and McLaughlin (16) have shown that self-diffusion and viscosity coefficients of ethyl iodide and n-butyl iodide, calculated by Bearman's equations agree with experiment to within 2% and that the mutual diffusivity of the system carbon tetrachloride - cyclohexane agrees with experiment within 0.5% over the complete composition range provided allowance is made for a volume change on mixing.

Laity (15) suggested the rather radical step of describing the diffusion process by the value of the friction coefficient rather than the diffusivity. He stated that the friction coefficient was independent of the motion of a reference plane. However his suggestion does not seem to have been accepted, judging from the Literature.

1.2.1 (d) Theory of Diffusion in Electrolyte Solutions

From the thermodynamics of irreversible processes, if the ions move independently, the Nernst-Hartley equation is obtained:

$$D_{12} = \frac{|Z_+ + 1 + |Z_- - 1}{|Z_+ + Z_- - 1} \frac{RT}{F} \frac{u^o_+ + u^o_-}{u^o_+ + u^o_-} \left[1 + \left(\frac{\partial \ln \gamma_\pm}{\partial \ln m}\right)_{T,p}\right] \quad ..(35)$$

where Z = valency of ion

F = Faraday

u^o = limiting ion mobility

γ = activity coefficient on molal scale

m = molality

Most of the variation of D_{12} with concentration is attributed to the activity factor, the residual variation is attributed to ignoring the effect of electrical interactions on the mobilities of the ions.

The "electrophoretic effect" states that as any ion moves it tends to drag other ions with it, the force being transmitted through the solvent molecules. It tends to increase the mutual diffusivity as both ions are moving in the same direction.

Hall, Wishaw and Stokes (18) who distinguished between solvent molecules attached in the hydration sphere and free solvent molecules, derived an equation for concentrated solutions of uni-univalent electrolytes which took the electrophoretic effect into account.

$$D_{12} = [D^o_{12} + \Delta_1 + \Delta_2]\left[1 + \left(\frac{\partial \ln \gamma_\pm}{\partial \ln m}\right)_{T,p}\right] \left[1 + 0.036\, m \frac{\eta_1}{\eta_{12}} \times \left(\frac{D^*H_2O}{D^o_{12}} - n_h\right)\right] \quad ..... (36)$$

where D^o_{12} = Nernst limiting value of D_{12}.

D^*H_2O = self diffusion coefficient of the solvent water.

n_h = an empirical hydration number chosen to give the best fit with experimental data.

Δ_1 and Δ_2 = electrophoretic effect corrections.

1.2.2. Semi-Empirical Approach

The method of Eyring (11) and Frenkel (7) was classed as semi-empirical because certain assumptions about the liquid state and the nature of the diffusion process were made. The following theory therefore, has not the same generality as the statistical mechanical theories.

Eyring's model of the liquid state was a disordered crystal lattice with holes floating in the liquid medium. Hildebrand (20) stated that experimental studies of the liquid state disagreed with the above model. Frenkel (7) stated that the increase, on melting, of the specific volume, indicated microscopic cavities and that the heat motion in liquids consisted in the vibration of atoms about equilibrium positions which changed with time. He postulated that after a large number of oscillations each atom jumped to a new equilibrium position at a distance λ, of the same order of magnitude as the mean distance between adjacent atoms.

Eyring's second assumption was that diffusion occurred through an activated state mechanism. Eyring's theory has been critically reviewed by MacDonald (10) and Bearman (14).

The final equations from MacDonald's summary were:-

$$D = S^2 \, Vf^{-1/3} \left(\frac{k\,T}{2\pi m}\right)^{\frac{1}{2}} \exp. \left(\frac{-E}{RT}\right) \quad \ldots\ldots\ldots\ldots (37)$$

and

$$\frac{D\eta}{k\,T} = \frac{\lambda 1}{\lambda 2\ \lambda 3} \quad \ldots\ldots\ldots\ldots (38)$$

where D = diffusivity; mutual in (37), self-diffusivity in (38)

Vf = the potential due to the presence of neighbouring molecules.

E = an activation energy per mole of diffusing substance.

$\lambda 1, \lambda 2, \lambda 3$ = distances in various directions between molecules.

MacDonald stated that equation (38) was exact only for self-diffusion in liquids as it assumed similar rate constants and activation energies for the processes of diffusion and viscosity. Olander (21) expanded and improved Eyring's equation. He gave as his starting point the equation:

$$\frac{D\mu}{T} = \frac{\lambda 1}{\lambda 2\ \lambda 3}\ \frac{k}{W}\ \exp.\ \left(\frac{\Delta F^{\ddagger}_{\mu} - \Delta F^{\ddagger}_{D}}{RT}\right) \quad \ldots\ldots\ldots (39)$$

where $\Delta F^{\ddagger}_{\mu}$ and $\Delta F^{\ddagger}_{D}$ are the free energies of activation of viscosity and diffusion respectively.

W = average number of nearest neighbours with respect to which the solute species moves. An empirical evaluation from mutual diffusion data gave $W = 5.6$.

Equation (39) was written in the form:

$$Y = \left(\frac{D\mu}{T}\right)\ \left(\frac{W}{k}\right)\ \left(\frac{V}{Nav}\right)^{1/3} = \exp.\ \left(\frac{\Delta F^{\ddagger}_{\mu} - \Delta F^{\ddagger}_{D}}{RT}\right) \ldots (40)$$

where V = molar volume of solute.

Nav = Avogadro's Number.

$(\Delta F^{\ddagger}_{\mu} - \Delta F^{\ddagger}_{D})$ was evaluated as follows:

At low solute concentrations the viscous mechanism is determined by the strength of the interactions between the solvent molecules. The process can be pictured as occurring in two stages:

(i) formation of a hole

(ii) movement of a neighbouring molecule into the recently vacated site.

The total free energy of activation for viscosity and self-diffusion is:

$$\Delta F^{\ddagger}_{\mu} = \Delta F^{h}_{AA} + \Delta F^{j}_{AA} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (41)$$

where ΔF^{h}_{AA} = activation energy to create a hole

ΔF^{j}_{AA} = activation energy to break a bond and overcome the repulsive forces.

But for mutual diffusion, the forces the solute molecule must overcome depend on the interaction between solute and solvent molecules.

Hence $\Delta F_D^{\neq} = \Delta F_{AA}^{h} + \Delta F_{AS}^{j}$ ..... (42)

Olander finally showed that

$Y = \exp(f\,d)$

where $d = \left(\frac{\Delta F^{\neq}_{AA}}{RT}\right) \left[1 - \left(\frac{\Delta F^{\neq}_{SS}}{\Delta F^{\neq}_{AA}}\right)^{\frac{1}{2}}\right]$ ..... (44)

$f = \frac{\Delta F^{j}}{\Delta F^{\neq}}$ and was calculated by Bondi to be 0.54

and $(\Delta F_{\mu}^{\neq} - \Delta F_D^{\neq}) = RT\,f\,d$ ..... (45)

He concluded that

Systems where $(\Delta F_{\mu}^{\neq} - \Delta F_D^{\neq})$ is positive give $Y > 1$.

Systems where $(\Delta F_{\mu}^{\neq} - \Delta F_D^{\neq})$ is negative give $Y < 1$.

1.2.3. Empirical Correlations

The main empirical correlations for diffusion coefficient have been reviewed by MacDonald (10). One correlation not covered is that of Gordon. Bearman, however, in his excellent review of diffusion theories, has shown that Gordon's equation is exactly equation (33) derived by statistical mechanical arguments.

The best known and most accurate empirical correlation is that of Wilke (22), who suggested a diffusion factor F, defined by the equation:

$$F = \frac{T}{D\eta} \quad \text{..... (46)}$$

Wilke proposed a solvent factor and prepared a chart from which the diffusion factor F for a solute of known molal volume diffusing in a known solvent could be estimated. The average deviation between predicted and experimental values was 10%.

1.2.4. Summary of all Correlations of Diffusivity

Equation (14) of Kamal & Canjar and equation (46) of Wilke are the correlations which agree best with experiment.

Wilke's equation is to be preferred on the grounds of accuracy but equation (14) has more theoretical background.

Also the development of Kamal & Canjar gives a prediction of the variation of diffusivity with concentration for the two cases, ideal and non-ideal solutions.

This equation agrees with that of Bearman and also with experiment.

1.3. Mass Transfer in Porous Media

1.3.1. Theoretical Studies

Although Prager (23) disagreed with the assumption of simplified models for a porous body and gave complex methods for calculating the effective diffusivity in inhomogeneous media where the actual diffusivity varied from point to point in a random manner, the most positive and easily verified approach used some model pore system. Akselrud (1) and Goodknight, Klikoff & Fatt (24) and (25) both used model pore systems.

Goodknight et al (24) claimed that the diffusion equation for transient flow to or from a porous substance must contain a term to account for that amount of fluid flowing into or out of the "dead-end pore volume". A brief resumé of their assumptions, arguments and conclusions will be given below.

Goodknight assumed that there were uniformly distributed pores which had only one opening to the main pore structure, that this opening was in the form of a neck of cross-sectional area A_o and length l_o, and that there was steady-state flow in the neck.

The porous medium considered had porosity ϕ_1, N dead-end pores of volume V_o. The system had a cross-sectional area A,

length L and tortuosity θ. Diffusion in an element of length d x was considered.

The difference between the diffusion flow in and out equalled the amount of solute stored in the element per unit time plus the amount of solute lost to "sinks" per unit time. Thus:

$$\frac{D\, A\phi 1}{\theta^2} \quad \frac{\partial 2\, C}{\partial x^2}\, dx = A\phi 1 \quad \frac{\partial C}{\partial t}\, dx + M^1 \quad \ldots\ldots\ldots\ldots (47)$$

where M^1 = diffusion flow in gm./sec. towards sinks.

$C(x, t)$ = concentration of solute.

If $C_2(x, t)$ = concentration of solute in sink.

and $V_2 = N V_c$

then $$M^1 = \frac{V_2}{L} \frac{\partial C_2}{\partial t}\, dx \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (48)$$

and $$M^1 = \frac{D\, A_o}{l_o} (C - C_2) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (48A)$$

With the conditions that there was no concentration gradient at the end of the pore length and that C_o was the initial uniform concentration Goodknight finally derived the equation:

$$C^1 = \frac{C - C_o}{C_1 - C_o} = 1 - \sum_{n=1}^{\infty} \left[\frac{\sin (2n-1) \frac{\pi x}{2L} \exp (S_n t)}{S_n L \left(\frac{\partial \beta}{\partial S}\right)_n} \right] \quad \ldots (49)$$

where $$S_n = -Y\left(1 + \frac{V_2}{V_1}\right) - \frac{D\beta^2}{2} \pm \frac{\left[\left\{Y\left(1 + \frac{V_2}{V_1}\right) + \frac{D\beta^2}{\theta 2}\right\}^2 - \frac{4\, DY\, \beta^2}{\theta^2}\right]^{\frac{1}{2}}}{2}$$

$$\beta = (2n - 1) \frac{\pi}{2L}$$

$$\left(\frac{\partial \beta}{\partial S}\right)_n = - \left\{1 + \frac{V_2}{V_1} \left(\frac{Y}{S_n + Y}\right)^2\right\} \frac{\theta 2}{D\, \beta_n}$$

$$Y = \frac{D\, A_o}{l_o\, V_c}$$

Goodknight et al claimed that equation (49) agreed with experimental evidence but this author considers it rather clumsy for chemical engineering use.

Barrer (26) had shown how the effective diffusivity of a gas could be measured by a time-lag method. Goodknight et al (25) showed that the diffusivity of liquids, calculated by the time-lag method was a function of the sum of the flow channel volume and the dead-end pore volume. The final equation was a comparatively simple expression:

$$T_L = \text{time-lag} = \frac{\left(1 + \frac{V_2}{V_1}\right) L^2}{6\alpha} \quad \ldots\ldots\ldots\ldots\ldots\ldots (50)$$

where V_2 = total volume of all dead-end pores;

V_1 = pore volume of flow channel;

L = length of porous medium;

α = effective diffusivity of the liquid.

Erdos and Jiru (27) considered mass transfer in porous media from another point of view. They compared the processes of diffusion with the conduction of electricity and concluded that, since the equations of the processes were formally similar, the diffusional characteristics of a porous material could be determined by measuring the resistance of an electrolyte in its pores. Their theories were complemented by experimental studies.

They stated that the classical law of free diffusion $Q = -D \operatorname{grad} C$ was similar to $J = -M \operatorname{grad} V$

where Q and J are fluxes of mass and electricity respectively.

D and M are coefficients.

and C and V are concentration and voltage respectively.

They also showed that for diffusion

$$\frac{q}{q_o} = \frac{\text{free flow}}{\text{hindered flux}} = \frac{A}{A_o} = \frac{\text{actual size of control surface}}{\text{geometrical size of control surface}} \quad \ldots\ldots (51)$$

and for electrical flow

$$\frac{I}{I_o} = \frac{\Lambda}{\Lambda_o} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (52)$$

where I and I_o were the free and restricted current fluxes.

Equations (51) and (52) were valid provided -

(i) interactions between fluid and porous material were negligible

(ii) the porous material was electrically non-conducting and

(iii) the dimensions of the pores were negligibly small of the radius of curvature of the control surface.

They defined Pd = q_+/q_o = diffusional conductance and $P_e = I/I_o$ = electrical conductance.

The conclusions of their experimental work with 0.05 - 0.20 N potassium chloride were as follows:-

(a) 'Isotropic' porous systems could be characterised by a single constant, "the conductance", which could be quickly measured by the electrical resistance of the electrolyte.

(b) $Pd = P_e$ Conductance was independent of the electrolute concentration.

(c) In diffusion through a layer of porous material, it was necessary to take account of the existence of a stagnant film whose influence was greater for very thin porous layers.

Conclusion (c) is the most interesting as it is the only reference to a boundary layer effect in the literature. P_e was always greater than Pd experimentally. Only when equations were derived for the stagnant film resistance, did Pd become equal to P_e.

The "conductance" has been considered by many workers. Petersen (28) reviewed theoretical attempts to predict the "conductance" or "diffusibility" from a knowledge of the porous material. For a porous system of uniform spheres, Maxwell gave: $\frac{D_e}{D_b} = \frac{2e}{3-e}$

where $\frac{D_e}{D_b}$ = conductance

and e = voidage or porosity.

For infinite cylinders normal to the direction of flow, Rayleigh gave:

$$\frac{D_e}{D_b} = \frac{e}{2 - e} \qquad \ldots\ldots\ldots\

Okromchedlidtse (31) working on the adsorption and desorption of tetralin and decalin on silica gels of different pore structures, reported that in all cases the flow rate had no effect on adsorption. The controlling function was stated to be the diffusion rate which depended linearly on the pore size, at least for mean pore radii up to 50Å.

The conclusions of the workers reviewed by MacDonald (10) were:

(1) Fick's 2nd Law fitted the experimental results quite closely.

(2) Initial solute concentration did not affect the rate of mass transfer.

(3) The solvent flow rate had no effect, i.e. there was no appreciable boundary layer resistance to mass transfer.

MacDonald (10), working on potassium chloride and sucrose, concluded that the sucrose was hindered more than the smaller potassium chloride and that the ratio $\frac{\text{diameter of diffusing entity}}{\text{mean pore diameter}}$ was important. He also concluded that for desorption the rate of mass transfer was independent of the initial solute concentration but was dependent for absorption. His results agreed with Crank's prediction of the relative rates of absorption and desorption.

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2. EXPERIMENTAL PROGRAMME

A programme of research was prepared, bearing in mind the following aspects of the problem.

2.1. The Nature of the Solute and Solvent

The properties of the solute which were investigated were the size, i.e. the diameter of the diffusing particle and the electrical properties i.e. whether the solute was an electrolyte or a non-electrolyte.

A correlation between the mutual diffusivity and the diameter of the diffusing species, including bound solvent, was sought.

The properties of the solvent which were considered were the size of the solvent molecule of to the size of the diffusing species and the chemical classification, i.e. whether the solvent was organic or inorganic.

Thus three solutes, one of which was an electrolyte, with different molecular diameters, were studied. Water was the solvent for two of the solutes and methanol, an organic compound, was the solvent for the third solute.

2.2 The Initial Concentration of the Solute

The dependence of the mutual diffusivity on concentration was so important that it was considered separately. Several workers have given solutions of the diffusion equation with a concentration-dependent mutual diffusivity. Their work is referred to in the mathematical section. The present experimental work dealt with concentrated solutions and the effect on the mutual diffusivity of large changes in the initial solute concentrations.

2.3. The Characteristics of the Porous Solid

The properties of the porous solid which affect the mass transfer of a fluid through its pores are:

(1) The porosity (% free volume).

(2) The mean pore diameter.

(3) The pore size distribution function.

(4) The shape of the pores, paying particular attention to the frequency of constrictions in the pores, and

(5) Chemical properties.

If there were a chemical interaction between the fluid and the porous solid, this interaction would obviously affect the rate of mass transfer.

The values of the mean pore diameter, quoted by the manufacturer were used, the porosity and pore size distribution were determined experimentally but the last two factors were not investigated. Empirical correlations between the mutual diffusivity and these factors were sought.

2.4. Flow Conditions in the Solvent

As reported in the introduction, section 1.3.2., most workers concluded that the boundary - layer resistance to mass-transfer was negligible. Only Erdos and Jiru (28) stated that the boundary-layer resistance was significant and became more important the thinner the layer of porous solid.

It was decided to conduct experiments throughout the laminar and turbulent ranges of Reynold's Number by varying the solvent flow rate and the relevant linear dimension.

2.5. The Nature and the Direction of Sorption

As stated in the introduction, section 1.1., Crank & Henry (5) predicted that where the diffusivity increased with increasing concentration absorption should take place more rapidly than desorption, and where the diffusivity decreased with increasing concentration the opposite should apply. It was decided to carry out absorption and desorption experiments to determine the effect of the porous solid in both cases.

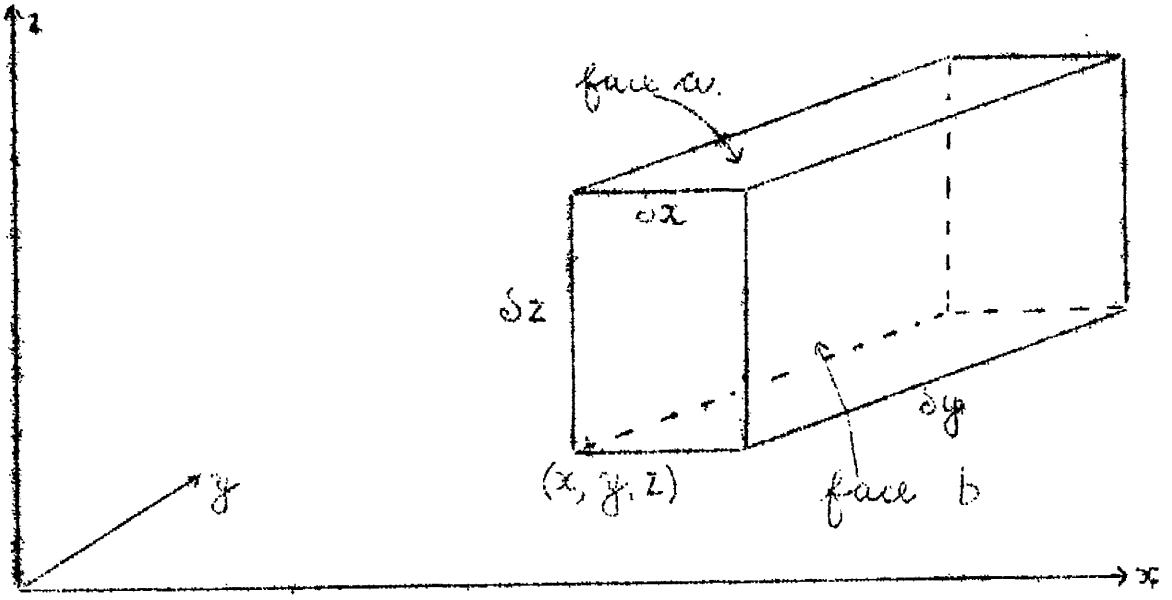
2.6. The Size of the Porous Material

It had been reported that the length of the diffusion path had an effect on mass transfer rates (see 2.4. above). The porous materials were made into cylinders of varying radius to investigate this effect.

3. THE MATHEMATICS OF DIFFUSION

The starting point of the theory was the equation of the continuity of mass. The mathematical treatment which is given below is based on the derivation given by Bird (32).

The flow of a multicomponent fluid through a small element of volume was considered.



Let p = density of the fluid at (x, y, z) at time t.

v = velocity of the fluid at (x, y, z) at time t.

p_i = density of the i th component at (x, y, z) at time t.

v_i = velocity of the i th component at (x, y, z) at time t.

v_{xi}, v_{yi}, v_{zi} = the components of v_i in x, y and z direction.

The mass of component i in the element of volume at any time is $p_i \, \delta x \, \delta y \, \delta z$.

The rate of change of this mass $= \frac{\partial p_i}{\partial t} \, \delta x \, \delta y \, \delta z$

In the absence of a source or sink (e.g. a chemical reaction) this rate of change of mass is due to the amount of the i th component flowing in not being equal to the amount flowing out in the same time.

Thus the net rate of increase across faces a and b

$$= p_i(x)\, v_{xi}\, \delta y\, \delta z - p_i (x + \delta x)\, v_{xi} (x + \delta x)\, \delta y\, \delta z$$

$$= - \left[\left(p_i \frac{\delta v_{xi}}{\delta x} + v_{xi} \frac{\delta p_i}{\delta x} \right) \delta x\, \delta y\, \delta z + \delta y\, \delta z\; 0 (\delta x^2) \right]$$

$$= - \frac{\delta}{\delta x} (p_i\, v_{xi})\, \delta x\, \delta y\, \delta z$$

Taking the flow across the other faces into account and equating to the rate of change of mass

$$\frac{\delta p_i}{\delta t} = - \left[\frac{\delta}{\delta x} (p_i\, v_{xi}) + \frac{\delta}{\delta y} (p_i\, v_{yi}) + \frac{\delta}{\delta z} (p_i\, v_{zi}) \right] \quad \ldots\ldots (1)$$

or in vector notation

$$\frac{\delta p_i}{\delta t} = - \nabla (p_i\, v_i) \quad \ldots\ldots (2)$$

Let u_i = the velocity of component i with respect to the local mass velocity v.

$$u_i = v_i - v$$

$$\text{or } v_i = u_i + v \quad \ldots\ldots (3)$$

$$\therefore \frac{\delta p_i}{\delta t} = - \nabla (p_i (u_i + v)) \quad \ldots\ldots (4)$$

$$= - \nabla p_i\, u_i - \nabla p_i\, v$$

$$\therefore \frac{\delta p_i}{\delta t} = - \nabla j_i - \nabla p_i\, v \quad \ldots\ldots (5)$$

where j_i is the mass flux vector and is the sum of four components:-

(1) j_i^c, the mass flux vector due to a concentration gradient (ordinary diffusion)

(2) j_i^p, the mass flux vector due to a pressure gradient (pressure diffusion)

(3) j_i^f, the mass flux vector due to a difference in external forces (forced diffusion)

(4) j_i^t, the mass flux vector due to a temperature gradient (thermal diffusion) (the Soret effect)

The forced diffusion term is only important in ionic systems and if gravity is the only external force the term vanishes identically.

The thermal diffusion term is important only in cases where there are very steep temperature gradients. Only the concentration term is important in the experiments carried out by this author.

The expression for j_i^c was derived by means of the Onsager relations in the thermodynamics of irreversible processes and the equations of momentum and energy. The assumptions used in deriving the expression were that the system was almost in equilibrium and that the fluxes were proportional to the first power of the gradients of the physical properties. The expression for the ordinary diffusion contribution to the mass flux vector was:-

$$j_i^c = \frac{C^2}{p\,RT} \sum_{j=1}^{n} M_i\, M_j\, D_{ij} \left[x_j \sum_{\substack{k=1 \\ k \neq j}}^{n} \left(\frac{\partial \bar{G}_j}{\partial x_k} \right)_{T,\, p,\, x_s} \nabla x_k \right]$$

$$S \neq k,\ j. \qquad \ldots\ldots (6)$$

where C = total concentration $= \sum_{i=1}^{n} C_i$

M_j = molecular weight of the j th component.

D_{ij} = mutual diffusivity of the i-j system.

x_j = mole fraction of the j th component.

$= \frac{p_j}{M_j}$

$\bar{G}_j$ = partial molar free energy (chemical potential) of the j th component.

The special case which deals with the experimental corditions in this researoh is:

Ordinary Diffusion in a Binary System

For two components A and B, equation (5) becomes

$$\frac{\partial p_A}{\partial t} = -\nabla j_a - \nabla (p_A v) \qquad \ldots\ldots (7)$$

and equation (6) becomes

$$j_A = \frac{C^2}{RT} M_A M_B D_{AB} \left[x_B \left(\frac{\partial \bar{G}_B}{\partial x_A}\right)_{T,p} \nabla x_A \right] \quad \ldots\ldots\ldots (8)$$

Using the Gibbs-Duhem relation, equation (9), and using equation (10)

$$x_A \, d\bar{G}_A + x_B \, d\bar{G}_B = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

$$G_A = G_A^o (T) + RT \log a_A \quad \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

where a_A = activity of A; equation (8) becomes:

$$j_A = -\frac{C^2}{p} M_A M_B D_{AB} \left(\frac{\partial \log a_A}{\partial \log x_A}\right)_{T,p} \nabla x_A \quad \ldots\ldots (11)$$

The activity factor in equation (11) takes into account the non-ideality of solutions.

For the purposes of simplicity, two assumptions were made:-

(1) The solution was ideal, i.e. the activity factor was equal to unity, and

(2) The solution was a system of constant mass density, i.e.

$$p = p_A + p_B = \text{a constant.}$$

Thus: x_A = mole fraction $= \frac{C_A}{C} = \frac{p_A/M_A}{p_A/M_A + p_B/M_B} = \frac{p_A M_B}{p_A M_B + p_B M_A}$

$$= \frac{p_A M_B}{p_A M_B + (p - p_A) M_A} = \frac{p_A M_B}{p_A (M_B - M_A) + pM_A}$$

and $$\nabla x_A = \frac{p M_A M_B \nabla p_A}{(p_A M_B + p_B M_A)^2} \quad \ldots\ldots\ldots\ldots\ldots (12)$$

$$\therefore \quad j_A = -C^2 \left(\frac{M_A M_B}{p_A M_B + p_B M_A}\right)^2 D_{AB} \nabla p_A \quad \ldots\ldots\ldots (13)$$

$$= -C^2 D_{AB} \left(\frac{1}{p_A/M_A + \frac{p_B}{M_B}}\right)^2 \nabla p_A \quad \ldots\ldots\ldots (14)$$

$$\therefore \quad j_A = -D_{AB} \nabla p_A$$

Substituting for j_A into equation (7)

$$\frac{\partial p_A}{\partial t} = \nabla(D_{AB} \nabla p_A) - \nabla(p_A v) \quad \ldots\ldots\ldots\ldots\ldots\ldots (16)$$

In a system where the net mass flow, v, is zero:

$$\frac{\partial p_A}{\partial t} = \nabla(D_{AB} \nabla p_A) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (17)$$

Finally, D_{AB}, is assumed to be constant.

Thus,
$$\frac{\partial p_A}{\partial t} = D_{AB} \nabla^2 p_A \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (18)$$

Equation (18) is Fick's Second Law.

In the derivation of equation (18), the following assumptions, which were made, are examined as to their validity.

(1) The solution is ideal.
(2) The mutual diffusivity is constant.
(3) The solution has a constant mass density.
(4) There are no "sink" or "source" functions.

Assumptions (1) and (2) are connected as the variation in mutual diffusivity with concentration is mainly due to ignoring the activity factor. The experiments were carried out with concentrated solutions which were certainly not ideal.

Assumption (3) was approximate as the experimental mass density did vary with time.

Regarding assumption (4), the equations of Goodknight et al (25) have been reviewed in section 1.3.1. It is probably incorrect to ignore the effect of "sink" or "source" functions.

Thus the examination of the four above assumptions, leads to the same conclusion, viz. Fick's Second Law can only be approximately true for the experimental conditions.

Several workers have suggested solutions of the general diffusion equation: $\frac{\partial C}{\partial t} = \text{div} \ (D \text{ grad } C)$ ..... (19)

Clarke (33) gave an approximate solution to equation (19) in terms of the error integral for the case when the diffusivity varied exponentially with the solute concentration, i.e.

$$D = D_o \ e^{a C}$$

Where D_o and a are the intercept and slope respectively of the graph of ln D against solute concentration.

From the results of English and Dole (34) and Gosting and Morris (35) Clarke stated that the differential diffusivity of sucrose in water decreased exponentially with sucrose concentration. In fact, their results show that the differential diffusivity decreased linearly with sucrose concentration.

Tsang (36) gave an approximate method of solving equation (19) in the case when diffusivity varies linearly with solute concentration and Helfferich (37) gave a numerical solution to equation (19) in the case when diffusivity varies according to the following equation:

$$D = D_o \ \frac{1}{1 + a \frac{C}{C_o}}$$

The solutions suggested were either approximate or numerical and hence difficult to interpret. Therefore, in view of the mathematical difficulties it was decided that the simpler Fick's Second Law would be used, with full knowledge that, at best, it could only be an approximation.

The equation for diffusion to or from a cylinder with ends closed by caps so that diffusion occurred in the radial direction only was:-

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \right) \quad \text{..... (20)}$$

where r is the general radius of the cylinder and with the conditions

(i) C finite as $t \longrightarrow + \infty$

(ii) C finite as $r \longrightarrow 0$

(iii) $C = 0$ when $r = a$ $\qquad (0 < t < + \infty)$

(iv) $C = C_1$ when $t = 0$ $\qquad (0 < r < a)$

By putting $C = R(r)\,T(t)$ (see appendix 1) the series solution, equation (21), was derived.

$$C = 2C_1 \sum_{S=1}^{\infty} \frac{1}{\alpha_S\, J_1(\alpha_S)}\, J_o\left(\alpha_S \frac{r}{a}\right) \exp. - \left(\frac{D\,t}{a^2}\,\alpha_S^2\right) \quad \ldots\ldots (21)$$

where C_1 = initial uniform solute concentration in the cylinder.

α_S = a typical root of the equation $J_o(\alpha_S) = 0$

J_o = Bessel Function of Zero Order.

J_1 = Bessel Function of First Order.

a = outer radius of the cylinder.

D = mutual diffusivity.

t = time.

The volume of a cylindrical element of unit length is $2\pi r\,dr$.

Let M = mass of solute in the cylinder at time t.

$$M = 2\pi \int_o^a C.\, r\, dr$$

$$= 2\pi\, 2C_1 \int_o^a \sum_{S=1}^{\infty} \frac{1}{\alpha_S} \frac{1}{J_1(\alpha_S)} \exp.\left(-\frac{D\,t}{a^2}\alpha_S^2\right) J_o\left(\alpha_S \frac{r}{a}\right) r\,dr \quad \ldots(23)$$

$$\therefore \quad M = 4\pi C_1 \sum_{S=1}^{\infty} \frac{1}{\alpha_S} \frac{1}{J_1(\alpha_S)} \exp.\left(-\frac{D}{a^2} t\, s^2\right) \int_o^a J_o\left(\alpha_S \frac{r}{a}\right) r\,dr \quad \ldots (24$$

Let the integral be I:

Let $x = r/a$

$$\therefore \quad I = \int_o^1 J_o(\alpha_S x)\, a^2\, x\, dx$$

Now $$\int_o^1 J_o(\alpha_S x)\, x\, dx = \frac{1}{\alpha_S}\, x.\, J_1(\alpha_S x)\Big|_0^1 = \frac{1}{\alpha_S} J_1(\alpha_S)$$

$$\therefore \quad M = 4\pi C_1 a^2 \sum_{S=1}^{\infty} \frac{1}{\alpha_S^2} \exp.\left(-\frac{D\,t}{a^2}\alpha_S^2\right) \quad \ldots\ldots\ldots\ldots (25)$$

M_o = the original mass of solute in cylinder of unit length.

$M_o = \pi a^2 C_1$.

$$\therefore \quad \frac{M}{M_o} = 4 \sum_{S=1}^{\infty} \frac{1}{\alpha_S^2} \exp. \left(- \frac{Dt}{a^2} \alpha_S^2 \right) \quad \ldots\ldots\ldots\ldots\ldots (26)$$

Crank (38) showed that, for short times, equation (26) could be simplified and written in the form

$$\frac{Mt}{M_o} = \frac{4}{\pi^{\frac{1}{2}}} \left(\frac{D}{a^2} \right)^{\frac{1}{2}} t^{\frac{1}{2}} - \left(\frac{D}{a^2} \right) t - \frac{1}{3\pi^{\frac{1}{2}}} \left(\frac{D}{a^2} \right)^{3/2} t^{3/2} \ldots (27)$$

where Mt = mass of solute which has diffused in time t.

Equation (27) and, to a lesser degree, equation (26), were used in modified form to calculate D, the mutual diffusivity, from the experimental results.

Although the detailed calculation of those properties necessary to determine the experimental value of the mutual diffusivity are given in the calculations section, it was thought wise to examine, at this stage, the effect of the solid structure on the diffusion process.

The solid structure causes the diffusing particle to follow a tortuous and longer path. The pore shape factor K^2, where K^2 is the ratio of the actual time to the theoretical time necessary to reach a given percentage extraction or K is the ratio of the actual to the geometrical distance travelled by the diffusing particle, was adopted to empirically determine the total effect of the solid.

K^2 is the same as the "conductance" suggested by Erdos and Jiru (27) but is more consistent with the fact that the square of the geometrical dimension appears in the exponential term of the solution to the diffusion equation.

4. EXPERIMENTAL METHODS

4.0 General Discussion of the Experimental Methods

Before considering the apparatus or the experimental technique in detail, a brief outline of the nature of the experiments will be given and then the function of each piece of apparatus will be described.

The two methods used to experimentally measure the rate of mass transfer of solute to or from a cylinder were:

(1) to measure the change of weight of the cylinder with time and
(2) to continuously measure the solute concentration at a point downstream of the cylinder.

In method (2), if accurate means of measuring both the solute concentration and the solvent flowrate were available then the rate of change of mass of solute with time, $\frac{dM}{dt}$, would be directly measurable and so, from this point of view, method (2) would be preferable to method (1) which did not give a direct measure of the rate of transfer of solute, since as the solute flowed into or out of the cylinder solvent flowed in the opposite direction.

Hence $\Delta W < \Delta M$

where ΔW = change of weight of the cylinder in time interval Δt

ΔM = mass of solute which has entered or left the cylinder in the time interval Δt.

By taking the change of density of the solution inside the cylinder into account equation (1) was derived (see section 5).

$$\Delta M = K . \Delta W \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where K = a constant for a particular solute-solvent system.

Method (2) was the more attractive method from a theoretical aspect but experience showed the comparative inaccuracy of the method of determining the solute concentration and most of the experimental results were obtained using the experimentally simpler method (1).

Experimental Procedure: The experimental procedure can be conveniently divided into three parts -

(1) Preparation of cylinders and analysis of the impregnating or circulating solution.

(2) Absorption or desorption of the solute under specified conditions.

(3) Total extraction of the cylinders at a high temperature.

Parts (1) and (3) are the same whichever method of measuring the rate of mass transfer is adopted in part (2). For this reason they will be considered first.

The experimental procedure is described in detail below.

4.1. A Detailed Description of the Experimental Procedure and Apparatus

4.1.1. The Porous Cylinders

The porous cylinders used were made from porous alumina silicate materials in three grades. These grades have been referred to by the manufacturer's catalogue numbers throughout the text. The physical dimensions and properties are given in Table 4.1.

The alumina silicate aggregate made up about 96% of the material and the remaining 4% consisted of clays used to keep the aggregate in suspension and to bond it during firing.

The cylinder ends were sealed by Teflon caps so that diffusion occurred only in a radial direction.

Table 4.1. Dimensions and Properties of the Porous Cylinders

Material (Catalogue Number)	Length (ins.)	Diameter (ins.)	Mean Pore Diameter (microns)	Pore Volume (%)
H.125	3	0.6; 0.5; 0.4	1.25	48
V.5	3	0.6; 0.5; 0.4	5	42.4
CC2	3	0.5; 0.4	0.67	32

The diameters of the cylinders are nominal but the exact diameter was measured with a micrometer. The mean of five readings was used in the diffusion equation. The value of the mean pore diameter was that quoted by the manufacturers as was the value of the percentage pore volume. The porosity or percentage pore volume was determined experimentally by this author. The author's values were, in general, higher than those quoted in Table 4.1., and there was a variation in porosity from one cylinder to the next in the same material.

Four properties of the porous media were determined experimentally and are described in detail below.

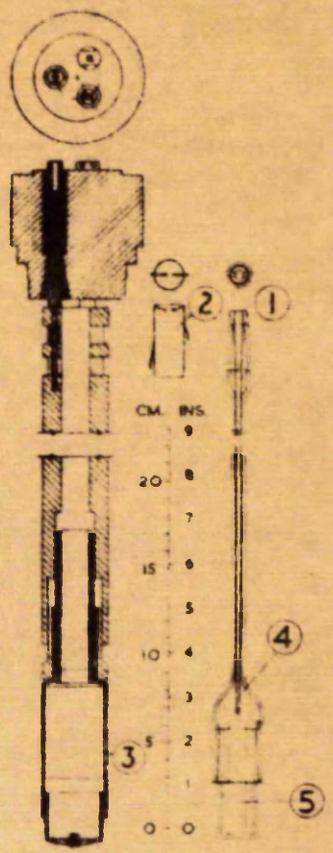
Determination of Total Pore Volume, Bulk Volume and Porosity

The total pore volume and bulk volume were determined by vacuum saturation of the porous cylinders with distilled water. The cylinders were dried in an oven overnight at 80°C, weighed and placed in a crystallising dish in a vacuum desiccator. The desiccator was connected to a vacuum system and evacuated to 0.2 mm mercury for one hour. Distilled water was then run on to the porous cylinders. After five minutes the system was opened to air and the cylinders were ready for measurement. The cylinders were weighed suspended in water, then placed in a dish at 100% humidity where the excess water rolled off. They were then weighed containing water. The calculations to obtain total pore volume, bulk volume and porosity are given in section 5.4.1. and the results in Appendix 3.

Determination of the Pore Size Distribution

The pore size distribution was determined using the mercury porosimeter at the Building Research Station, Garston, Herts. The mercury porosimeter will be described in some detail below (39).

Principle: The operative principle is that mercury is forced into the voids in a previously evacuated specimen, against the resistance of surface tension forces. The pressure required to fill any void is a function of the diameter of the largest entrance to that void. A plot of mercury



(1) DILATOMETER.
(2) PERSPEX SLEEVE.
(3) HOLDER.
(4) PLATINUM-IRIDIUM WIRE.
(5) SAMPLE.

Fig. 1. 63.167.1

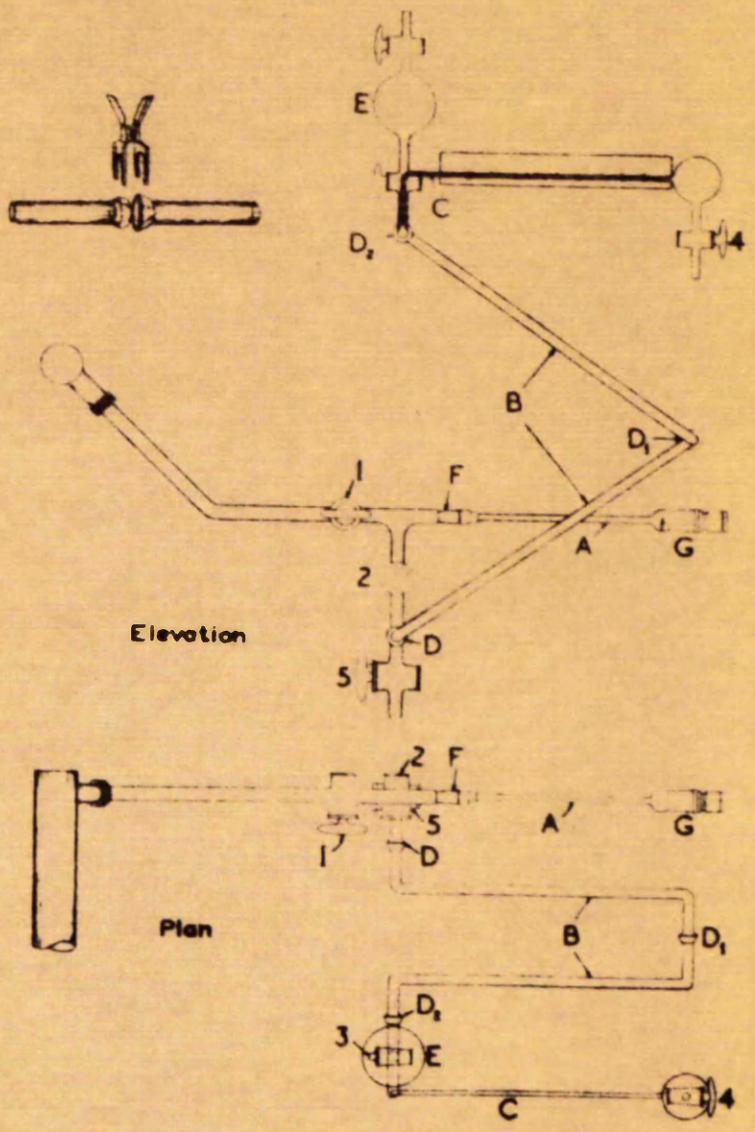


Fig. 2. 61.157.2

entering the specimen against applied pressure will therefore give a picture of the pore entry dimensions and (though by inference only) some idea of the distribution of actual pore sizes.

Apparatus: The determination is done in two stages, low pressure and high pressure, representing respectively coarse and fine pores. The same dilatometer is used throughout.

Dilatometer Fig. 1.

This is essentially a capillary with a specimen chamber (closed by a glass stopper) at one end, and a conical glass joint at the other. A loop of platinum/iridium resistance wire (4) is stretched inside the capillary, and is terminated as two platinum contacts fused into the periphery of the ground glass joint.

Low Pressure Apparatus Fig. 2.

This consists essentially of a flexible U-tube of glass, one arm of which is the dilatometer (A) connected via a 3-way glass manifold and the movable arm (B) to a calibrated capillary tube (C). The mobility of B is obtained by using three spherical glass joints (D, D_1, D_2) held together by spring clips (inset Fig. 2). This enables the tube C to be raised above the specimen in the dilatometer. A reservoir (E) supplies mercury to the whole system, including the dilatometer, after evacuation through tap 1. In use, the pressure on the sample is altered by varying the height of the capillary relative to the dilatometer. The volume of mercury entering the sample is then measured on the capillary.
Range: 0.5 cm Hg to 105.5 cm Hg (20 lb./sq. in.) corresponding to : 2000 to 10.5μ pore entry diameter.

High Pressure Apparatus Fig. 3

This is a stainless-steel bomb into which the dilatometer, in a tufnol carrier, is placed.

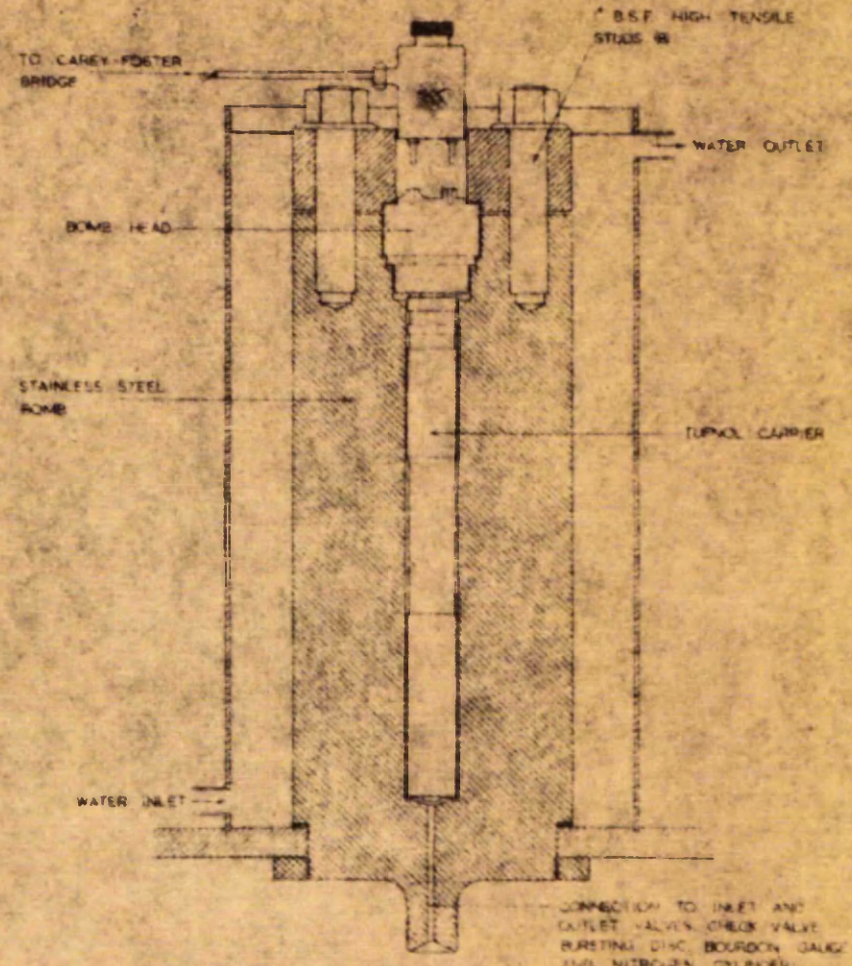


Fig. 3. C13671.1

A perspex sleeve ([2] in Fig. 1) makes electrical contact between the platinum/iridium resistance wire in the dilatometer and a three pin socket in the bomb head. Increasing pressures are then applied by allowing successive charges of nitrogen, from a cylinder, into the bomb. The amount of mercury entering the specimen is followed by measuring the change in resistance of the platinum/iridium wire. Two nitrogen cylinders are used, one for the greater part of the run and an almost new cylinder for obtaining the top pressure of 1800 lb./sq. in.

Range: 20 lb./sq. in. to 1800 lb./sq. in. corresponding to: 10.5 to 0.12μ pore entry diameter.

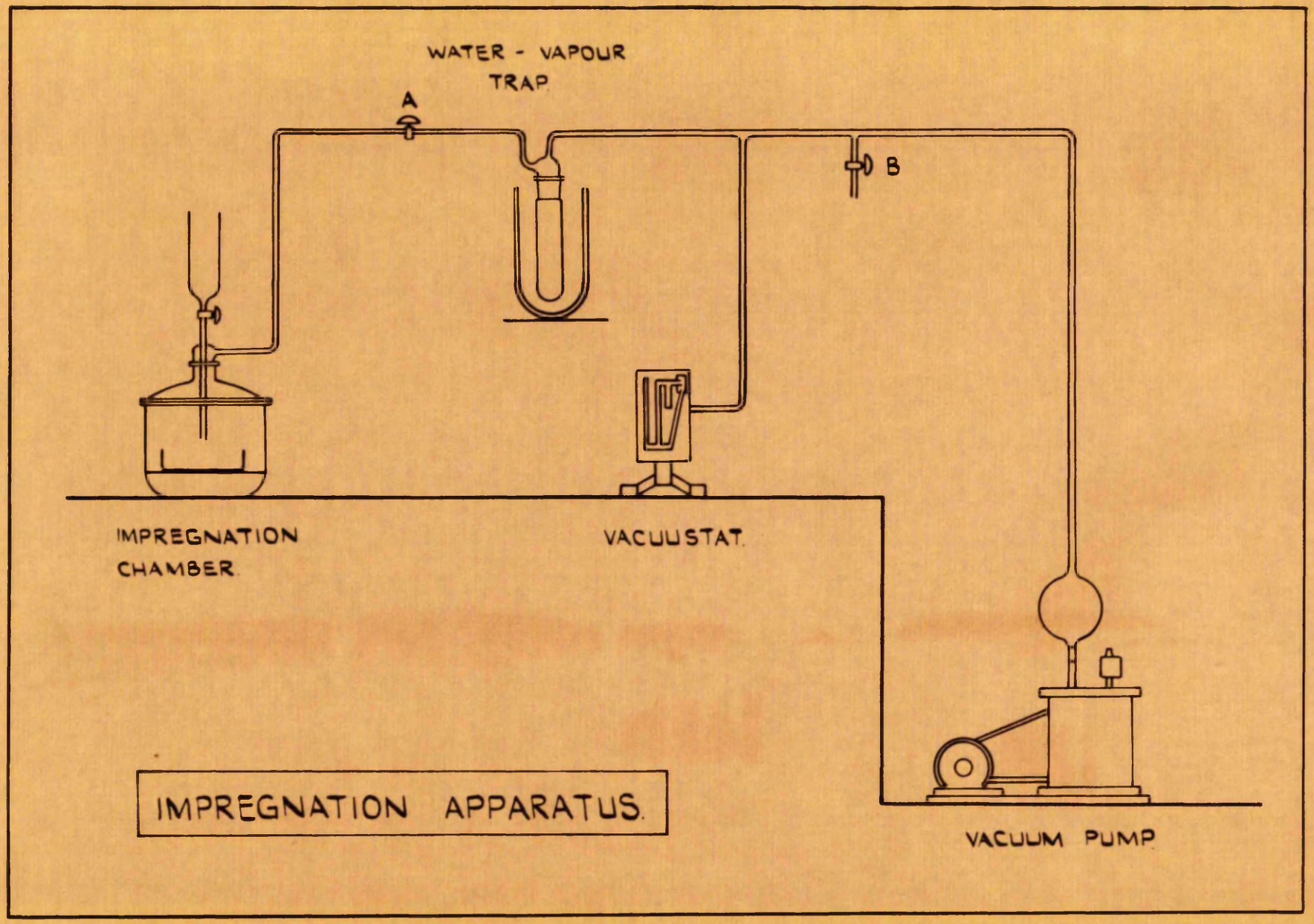
The lower pressure is that at which the low pressure apparatus left off: it equals atmospheric pressure plus the pressure due to the column of mercury in the dilatometer capillary.

The calculations for the mercury porosimeter are given in section 5.4.2. and the results of the experiments are given in Appendix 3.

4.1.2. <u>The Solute-Solvent Systems</u>

Brief mention will be made here of the ancillary work carried out to determine the properties of the solute-solvent systems which affect the mutual diffusivity in porous media. The properties considered were the mutual diffusivity in free solution, the molecular diameter and the value of 1/k (see 5.3.).

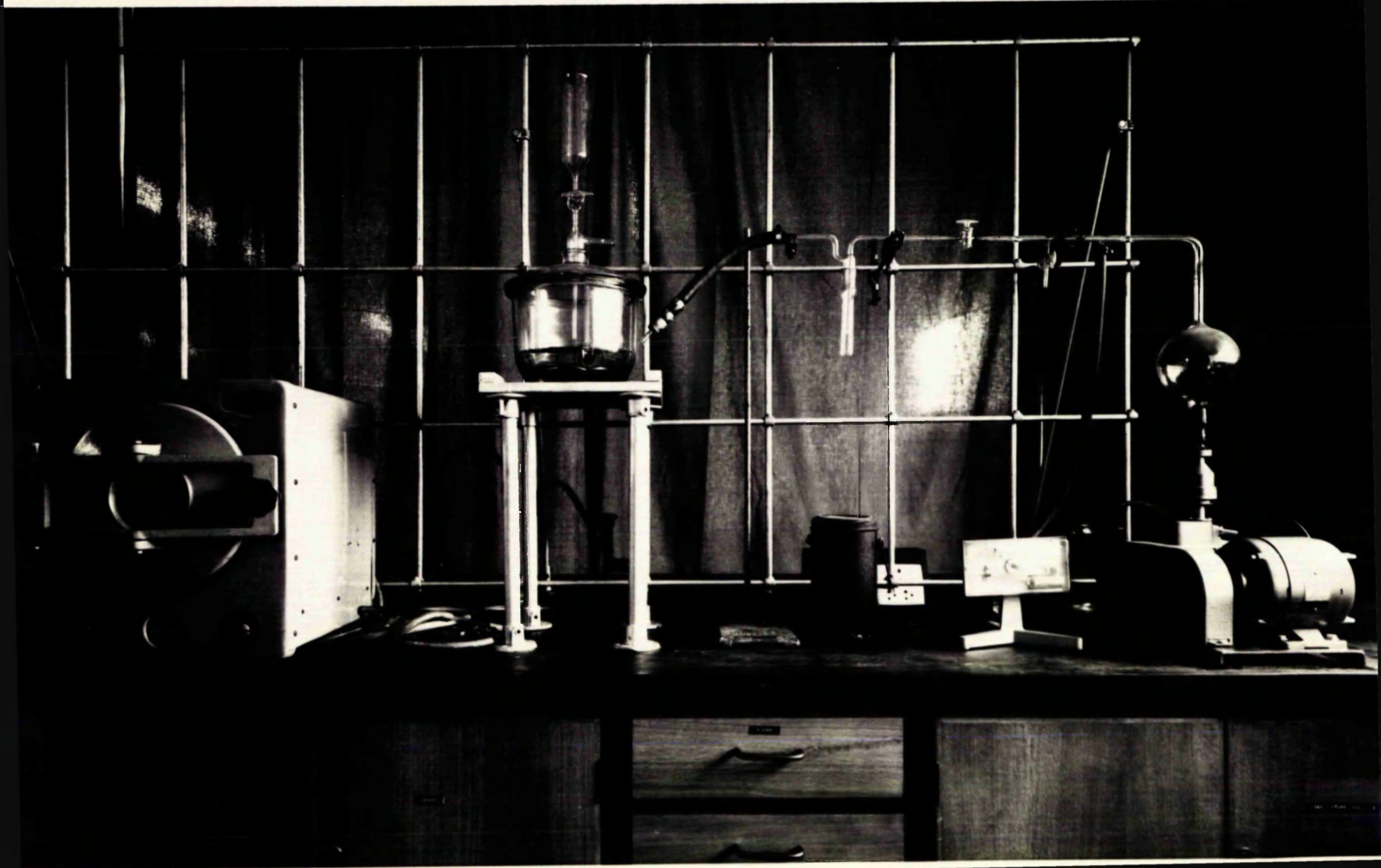
The mutual diffusivity in free solution and the value of 1/k were obtained from the literature. The molecular diameters of potassium chloride and carbon tetrachloride were also obtained from the literature. The molecular diameter of sucrose was obtained with the help of a scale model. Tabulated values of these three properties are given in Appendix 2.



IMPREGNATION APPARATUS.

FIG. 4.

Fig. 4A



4.1.3. Preparation of the Porous Cylinders

When not in use the cylinders were immersed in distilled water to prevent dirt entering the pores. Before use the cylinders were washed with distilled water and dried in a vacuum oven at 80°C. and 30 ins. mercury vacuum to constant weight.

After weighing in tared aluminium tins, the cylinders were placed in a crystallising dish in the vacuum desiccator (see Figs. 4 and 4a) which was then evacuated by a vacuum pump. When a vacuum of approximately 0.05 mm mercury had been held for thirty minutes, tap A was closed and the impregnating solution (either a solution of the solute or pure solvent) slowly run on to the cylinders under vacuum. Tap B was opened to release the vacuum in the rest of the system. After five minutes tap A was opened to air.

The cylinders were ready for extraction purposes. The cylinders were taken as required. At the time when a cylinder was removed for extraction, the temperature and concentration of the solution (for desorption) was determined. In the case of absorption experiments the temperature of the impregnating pure solvent was taken and the concentration of the circulating solution was determined.

The methods of determining the solute concentration in either the impregnating or the circulating solution are described in the next section.

4.1.4. Determination of the Weight Fraction of Solute in either the Impregnating or the Circulating Solution

The initial solute concentration in the porous cylinders (for desorption experiments) or the solute concentration in the circulating solution (for absorption experiments) must be determined for two reasons:-

(1) Comparison between experiments at different concentrations, and

(2) Determination of M_o, the mass of solute initially in the cylinder (for desorption experiments) or of M_∞, the mass of solute absorbed by the cylinder after infinite time (for absorption experiments).

Three solute-solvent systems were examined. As the analysis to determine the weight fraction of solute in the solution differed with each system, the methods of analysis were considered separately.

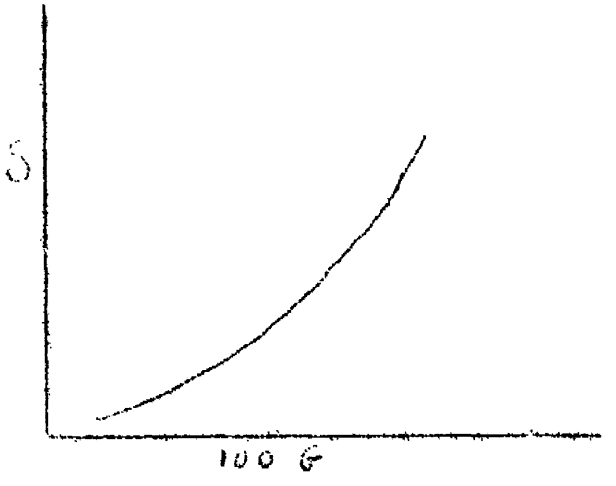
4.1.4(a). Determination of the Weight Fraction of Potassium Chloride in Aqueous Solutions

The concentration (gm./ml.) of potassium chloride was determined volumetrically by titration with standard silver nitrate using potassium chromate solution as indicator. The silver nitrate had been previously standardised against a potassium chloride solution, carefully prepared on a weight basis.

The potassium chloride solution was titrated until the solution turned faint salmon pink. Details of the analysis are given in Vogel (40).

The weight fraction was determined from a graph of S against 100G.

The values of weight fraction, density and concentration were taken from International Critical Tables.



S, G and X are related by the equation

$$X = 100\,G - S \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where X = weight percentage

G = gm./ml. (from titration)

and S is defined by equation (2)

CALIBRATION CURVE OF CARBON TETRACHLORIDE

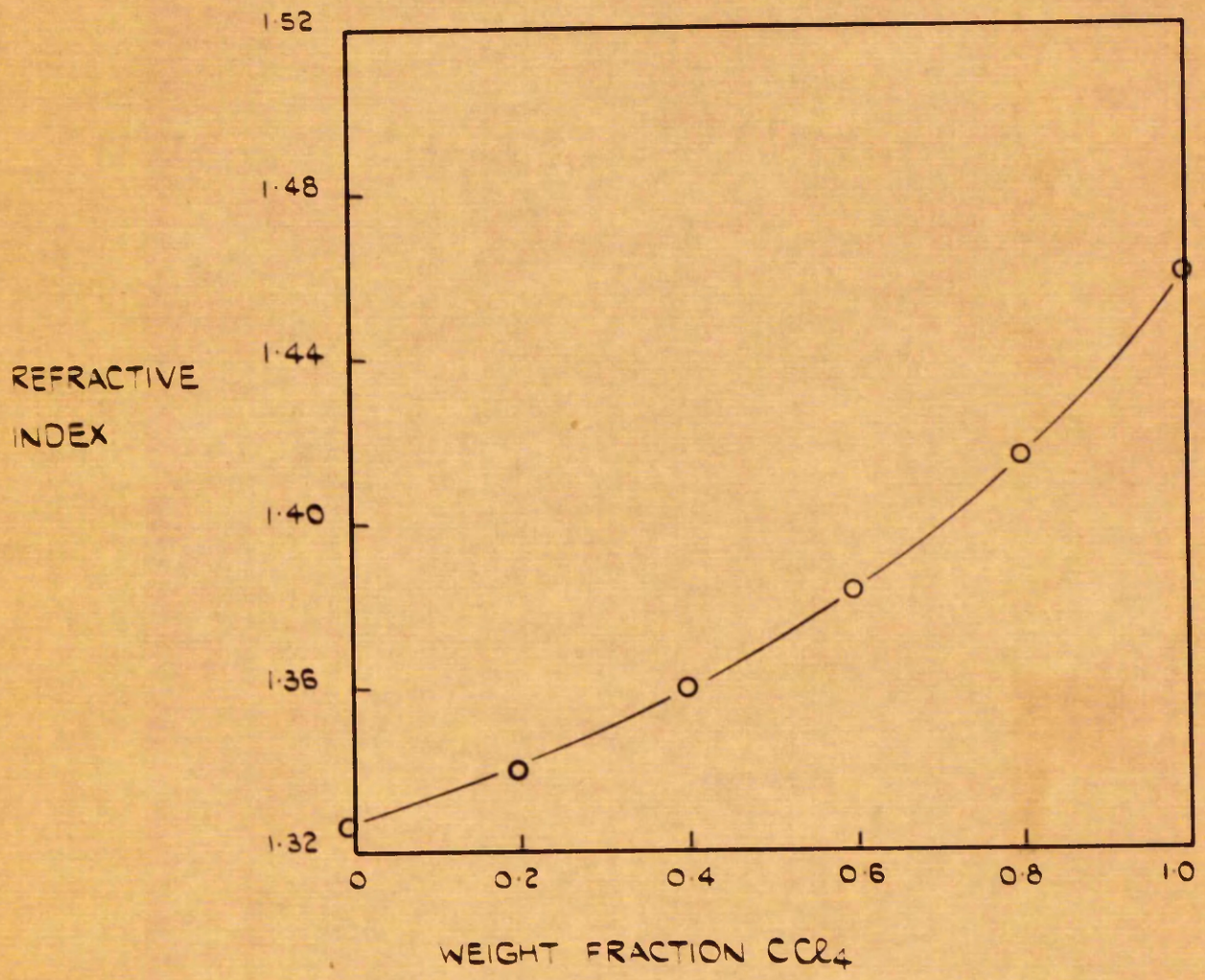


FIG. 5.

4.1.4(b). Determination of the Weight Fraction of Sucrose in Aqueous Solutions

The concentration of sucrose (gm./ml.) was determined by polarimetry.

The specific rotation, $[\alpha]_D^{20}$, with sodium lamp at 20°C, was given as 66.4, (41) and (42).

The sucrose concentration was calculated from equation (3)

$$[\alpha]_D^{20} = \frac{\alpha}{l \cdot c} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where α = observed rotation in circular degrees

l = length of solution in decimetres

c = concentration in gm. sucrose/ml.

The polarimeter tube used was 2 decimetres long and so equation (3) reduced to

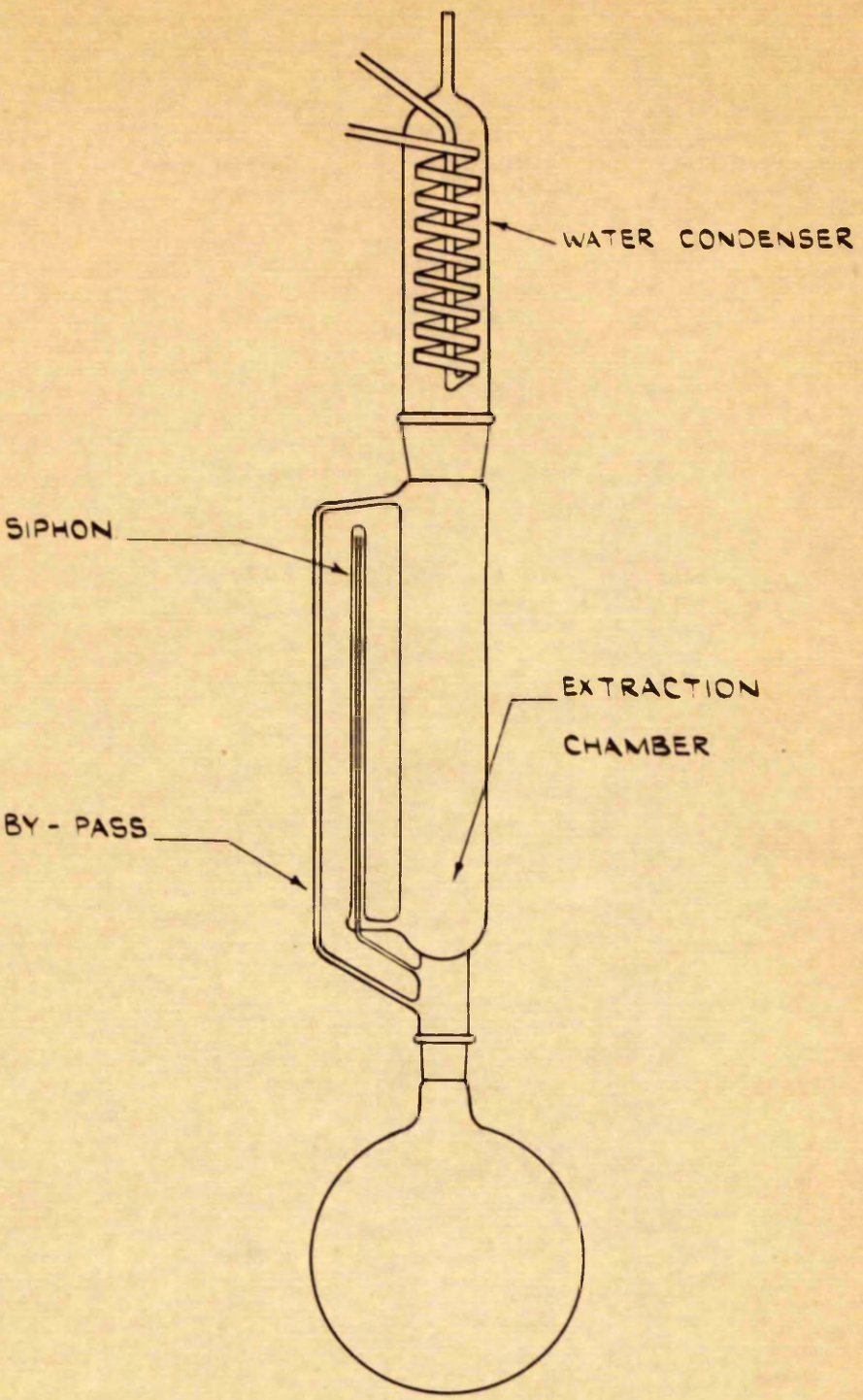
$$c = 0.00754 \alpha \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

From a graph of density of sucrose solutions at 20°C. against concentration (determined by polarimetry), the weight fraction of sucrose was determined from equation (5).

$$\text{Wt. fraction} = \frac{\text{concentration } 20^\circ\text{C}}{\text{density } 20^\circ\text{C.}} \quad \ldots\ldots\ldots\ldots \quad (5)$$

4.1.4(c). Determination of the Weight Fraction of Carbon Tetrachloride in Solutions of Methanol

The weight fraction of carbon tetrachloride in methanol solution was determined by the refractive index of the solution. The value of the refractive index found was referred to a calibration curve (fig. 5) of refractive index against weight fraction and the weight fraction was read off directly.



SOXHLET EXTRACTION APPARATUS

FIG. 6.

4.1.5. Total Extraction of the Cylinders

Since no solute must remain in the cylinders for subsequent runs, after the absorption or desorption experiments the cylinders were totally extracted by one of two methods, depending on the solute-solvent system.

In the case of the system, carbon tetrachloride-methanol, it was sufficient to heat the cylinders in the vacuum oven for six hours. All the vapour was driven off in this period.

The extraction of the aqueous solutions of potassium chloride and sucrose took place in the Soxhlet extraction apparatus, shown in Fig. 6.

The porous cylinders were placed in the extraction chamber and the flask half-filled with water. The flask was heated by an electric heating mantle and the steam passed via the by-pass tube to the condenser and condensed into the extraction chamber. When the solution in the chamber reached the level of the siphon, the solution was siphoned off via the side tube, and the cycle recommenced.

Extraction for six hours was sufficient to completely remove the solute from the porous cylinders.

4.1.6. Apparatus and Experimental Techniques used to Study the Diffusion Process

Two techniques were used to study the diffusion process:-

(1) Measurements of the change of weight of the porous cylinder with time using a recording balance;

(2) Measurement of the solute concentration downstream of the cylinder by a capacitance cell.

Methods (1) and (2) will be described in detail below.

Method (2) was used as a check on method (1).

FLOW DIAGRAM FOR EXPERIMENTS WITH RECORDING BALANCE

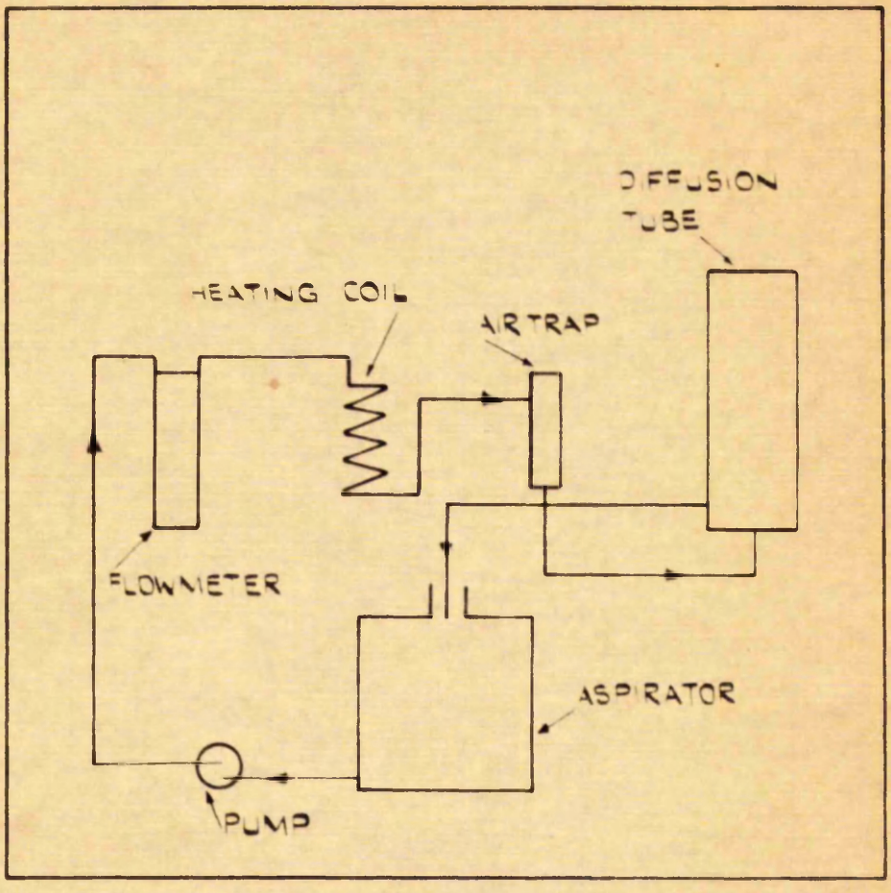
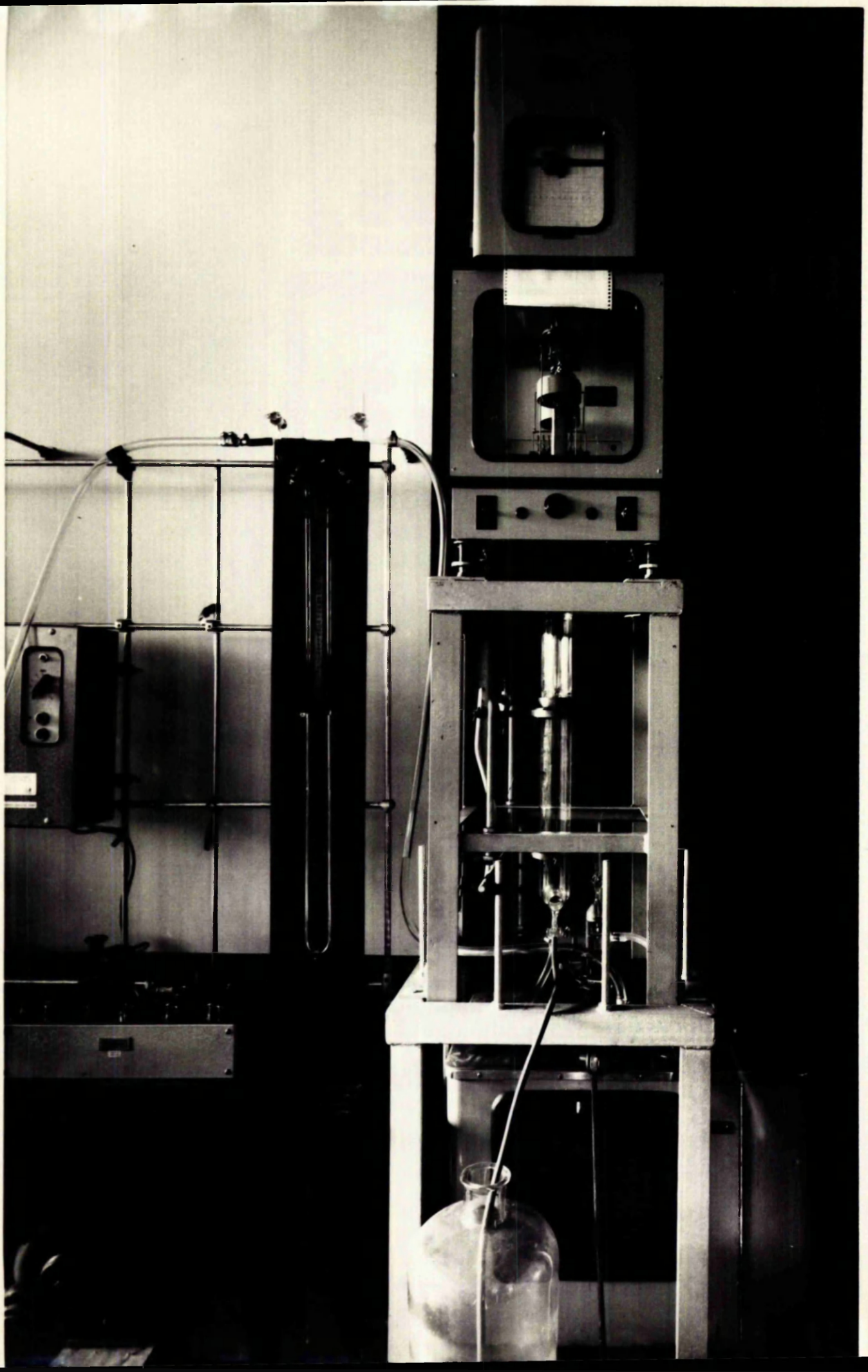


FIG. 7



4.1.6.1. Measurements of Absorption or Desorption using the Recording Balance

The arrangement of the apparatus used in the study of the diffusion process is shown in Figs. 7, 7a.

The Flow System

Note: In desorption experiments, the "liquid" was pure solvent; in absorption experiments it was a solution of the appropriate concentration.

The liquid was pumped by a positive displacement stainless-steel pump from the glass aspirator to a glass constriction where the flowrate was measured by a mercury manometer. The liquid then flowed through two glass heating coils and an air-trap (all immersed in the constant temperature water bath which was controlled at 25°C), through the diffusion tube and back into the aspirator.

Many of the earlier experiments were carried out with an open flow circuit, i.e. the solvent flowed to waste when it left the diffusion tube. This method would, of course, be most wasteful if carried out for absorption experiments. It was shown that with the closed system air bubbles disappeared after a few minutes.

The air bubble effect had been a source of trouble with the open system and so all the experiments from that time were carried out using the recycle or closed system.

The Diffusion Tube

The diffusion tube is shown in detail in Fig. 8.

The liquid flowed into the diffusion tube by the inlet, continued up the inner glass tube, past the porous cylinder which was suspended from the recording balance by a fine wire, over the weir, down the outer annulus and back to the aspirator via the outlet.

THE DIFFUSION TUBE

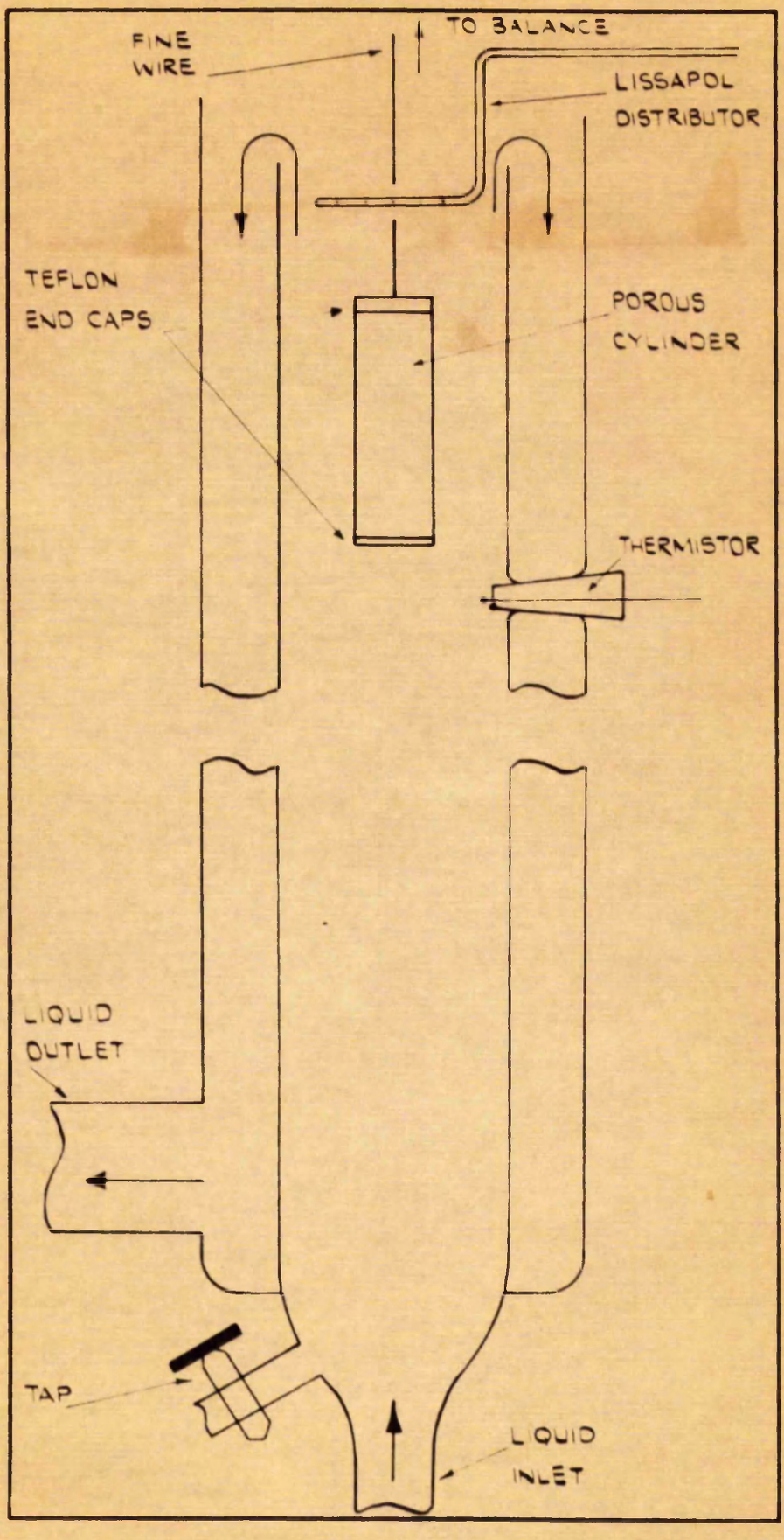


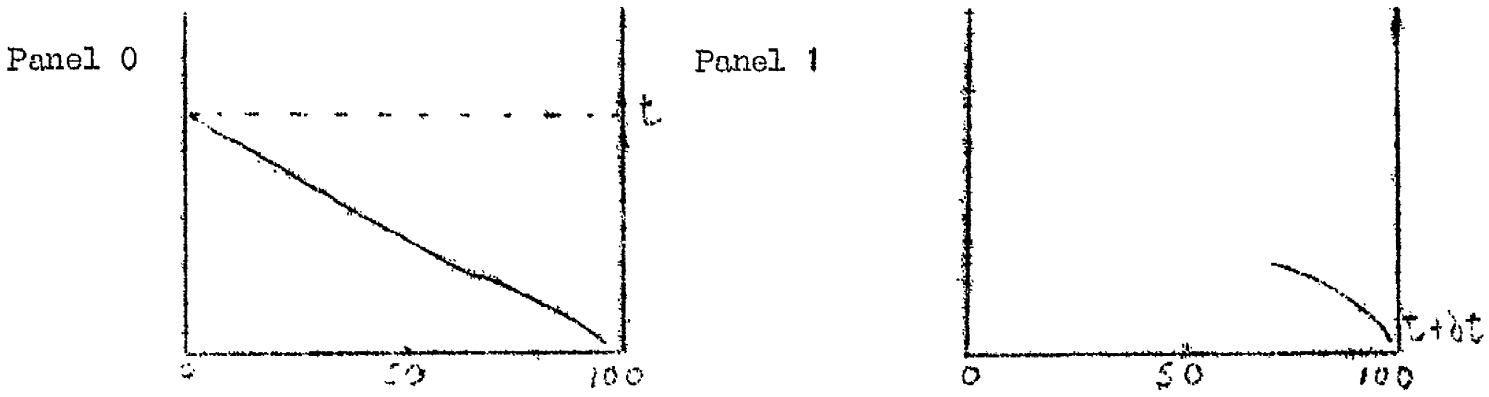
FIG 8.

The Recording Balance

The apparent weight of the porous cylinder was shown by the chart above the recording balance. (See Fig. 7a).

The balance has two pans. From one pan a fine wire is suspended by a hook. The other end of the fine wire consists of a 6BA thread which screws into the upper Teflon cap of the porous cylinder. Weights are placed on the other pan to give an "on-scale" reading on the chart.

A desorption run will be considered to demonstrate how the balance works. Since a loss of weight is known to occur the "Loss-Loss" model is used. When the balance has removed 10 mg. a "weight change" occurs, the figure 1 appears on the balance panel and the chart pen moves full scale.



Since there are eighteen "weight changes", the balance can show a total weight change of 180 mg. without changing the large weights in the pan.

The opposite procedure occurs when a gain of weight occurs. The "Gain-Gain" model is used and a gain of 180 mg. can be recorded without changing the large weights in the pan.

The Solution Temperature

The stream temperature of the liquid in the inner tube was measured by a thermistor inside a rubber stopper. The thermistor, previously calibrated against a sensitive mercury thermometer, lead to

a Wheatstone bridge circuit in which the balancing resistance to give zero galvanometer reading was a measure of the temperature.

Experimental Procedure

The pump was switched on and liquid flow was maintained until the stream temperature was constant at 25°C. A porous cylinder, whose weights dry and containing the impregnating solution had been noted, was suspended from the recording balance hook. The tap at the bottom of the diffusion tube which had been opened just before the porous cylinder was ready to be suspended, was closed, and the circulating liquid began to flow up the inner tube. When the liquid reached the bottom of the porous cylinder the time chart mechanism was started.

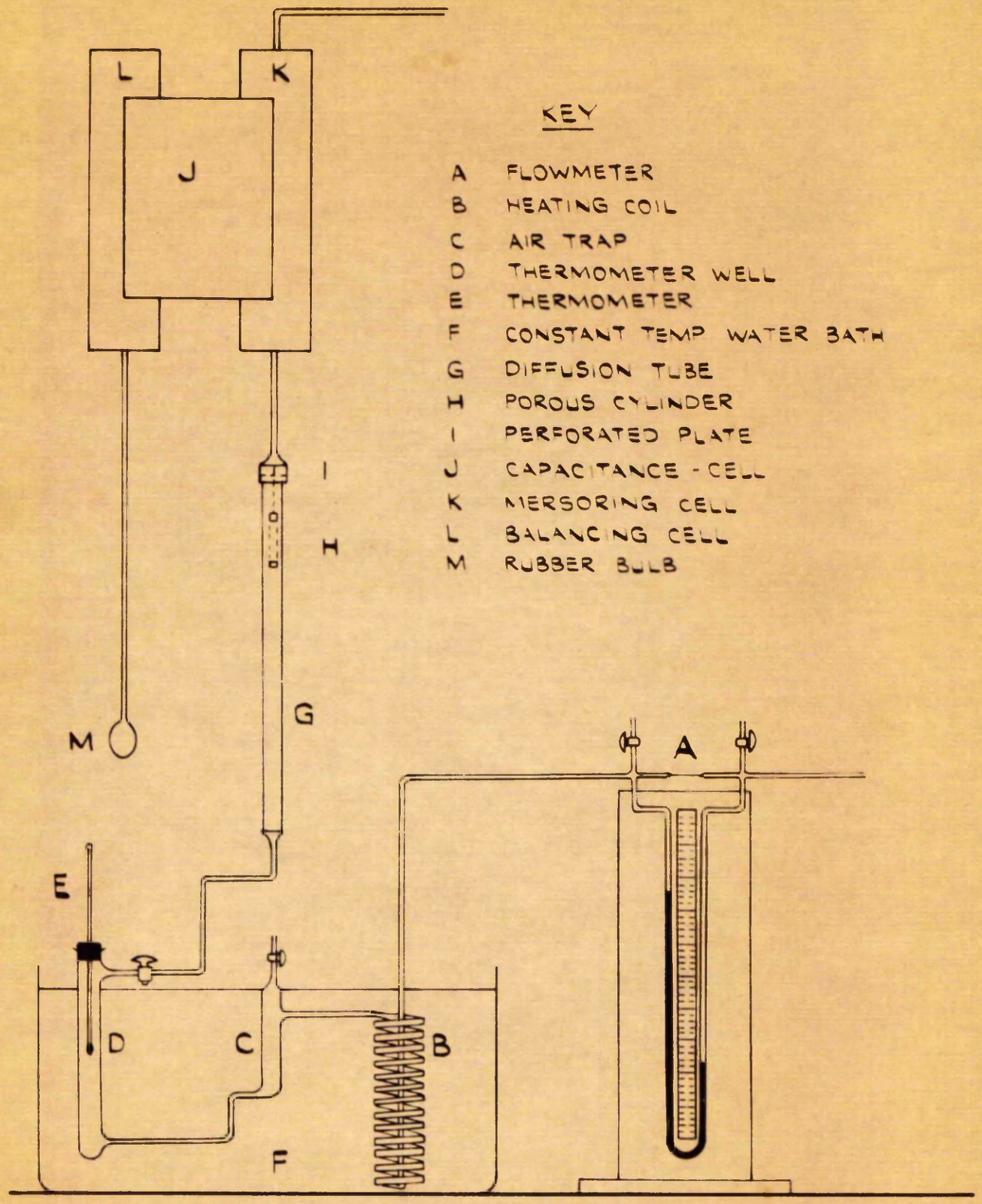
The approximate balancing weights, learned by experience, were placed in the balance pan, the balance turned to "action" and the weight in the pan adjusted until a reading was obtained on the chart. An "on-scale" reading was usually obtained in less than three minutes. The balance was then turned to "operate" and was completely automatic.

After a certain period of time, (the calculation of this time interval is given in section 5) the balance was turned to "arrest", the flow was stopped and the porous cylinder removed and placed in distilled water, ready for total extraction.

The experimental technique using this method was relatively simple and there were only two difficulties of any importance.

The first attempts to measure cylinder weight changes were made by suspending the cylinder from the recording balance by a solid rod, 1/16" diameter. The recorder chart showed discontinuities and it was decided that the surface tension force, which acted against the weight change, was preventing the balance from picking up weight changes if they were below a certain finite value. Two methods of remedying this were proposed:

(1) Use of a very fine wire, diameter 44 s.w.g.



ARRANGEMENT OF APPARATUS USED IN THE STUDY OF THE DIFFUSION PROCESS

FIG 9.

(2) Use of a spray of lissapol (a commercial wetting agent) near the liquid surface.

The lissapol was sprayed just under the liquid surface by means of the lissapol distributor ring. (See Fig. 8).

Experiments at different lissapol flowrates were carried out. The results varied in such a random and arbitrary manner with lissapol flowrate that it was feared that the lissapol was interfering with the mass transfer process itself, besides reducing the surface tension. It was also found that for large cylinders at dilute solute concentrations and for the smaller cylinders at higher concentrations the lissapol had no effect on the rate of mass transfer.

Thus it was decided to use longer porous cylinders and to carry out all further runs without lissapol.

The second difficulty was of ensuring that changes in the apparent weight of the cylinder were due only to the occurrence of mass transfer. The apparent weight would change if the liquid flowrate changed or if air bubbles collected on the cylinder and thus affected the upthrust.

The flowrate changed very little but air bubbles did appear immediately when the flow was started. The bubbles were removed by gently tapping the cylinder and when the closed flow system was adopted the problem became almost negligible except at very high flowrates when air was introduced into the suction side of the flow circuit.

4.1.6.2. Measurement of Desorption using the Capacitance Cell

The arrangement of the apparatus is shown in Fig. 9.

The desorption took place in the copper diffusion tube (G). The porous cylinder (H) was suspended from a perforated plate (I) which also served to mix the solution leaving the tube.

The de-aerated distilled water used to carry out the desorption was pumped from a large polythene reservoir via the flowmeter (A) to a

copper temperature coil (B) where the water attained the temperature, 25°C, of the constant temperature water bath (F). From the coil, the water proceeded via the air-trap (C) and thermometer (D) to the diffusion tube (G) where desorption took place. The solution leaving the diffusion tube then flowed to the detecting element (K) of the capacitance cell (J) which measured the concentration of the solution. The solution leaving the capacitance cell finally flowed to waste.

During calibration runs, the calibrating solutions of potassium chloride were passed from the thermometer well (D) to the detecting element (K) via a by-pass line. The flowmeter (A) was also by-passed.

These by-passes were precautions so that no potassium chloride remained in the flow system and came out subsequently during an actual diffusion experiment.

One calibration solution was passed through the system before each diffusion run to make sure that the instrument calibration had not changed. The system was then washed with distilled water for an hour and the system was ready for a diffusion experiment.

It should be noted that this apparatus could be used for desorption only since the capacitance cell was designed to measure very small concentrations. Also only the system potassium chloride-distilled water was examined using this apparatus.

The capacitance cell circuit will be described in detail below.

The Capacitance Cell Circuit

The pioneering work on using a capacitance cell to measure continuously the concentration of an electrolyte solution was carried out by Little and MacDonald (43).

Much work went into the development of the capacitance cell circuit. There have been many modifications to the electrical circuit and so only the final circuit used will be described below.

The principle of the method is that when an alternating voltage

is applied to a condenser consisting of a glass tube, through which liquid is flowing the alternating current passed by the condenser is a function of the concentration of the flowing liquid.

The alternating current was rectified, applied to a resistance and the voltage thus generated appeared as a deflection on a recorder.

Thus the recorder deflection was a function of the concentration of the electrolyte solution.

General Description and Use of the Capacitance Cell

The capacitance cell used to measure the potassium chloride concentration downstream of the porous cylinder consisted essentially of a glass tube sheathed with two brass electrodes.

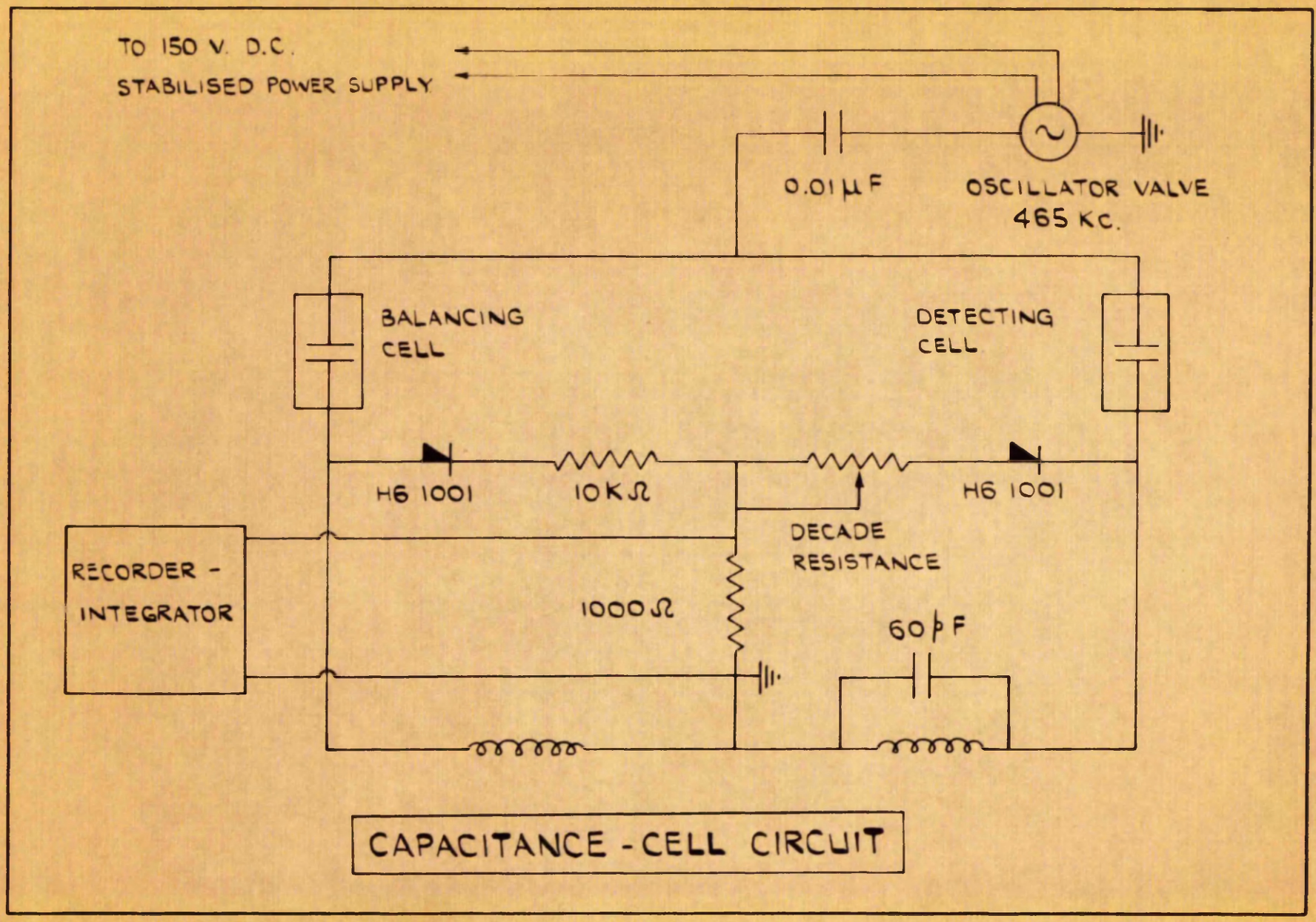
Two identical cells were included in the capacitance cell circuit, one of which, (the "balancing" cell), was permanently filled with distilled water, the other being the actual detecting element through which the solution flowed.

Before being used for actual concentration measurements, the circuit was balanced by passing distilled water through the detecting cell and adjusting the value of the decade resistance until the output from the circuit was zero (as shown by the recorder).

During diffusion experiments, with potassium chloride flowing through the detecting element, the current passed by the detecting cell was greater than the current passed by the balancing cell and hence an out-of-balance e.m.f. was generated, which was measured on the recorder.

The recorder was fitted with a number of doubling scales and a system of shunts (described in detail below) which enabled a suitable fraction of the e.m.f. to be used to activate the recorder, so that a recorder deflection of between 50% and 100% full scale deflection (F.S.D.) could always be obtained.

The recorder also included a numerical integrator whose rate of counting was proportional to the recorder deflection. To bring all



CAPACITANCE - CELL CIRCUIT

FIG. 10.

readings to a common basis, the integrator counting rate (in counts per minute) had to be multiplied by the scale value and divided by the shunt value. (The relative values of the shunts and scales are given in Table 4.2).

Thus the recorder factor $\frac{CN}{S}$ was calibrated against a series of potassium chloride solutions of known concentration.

C = counts per minute.

N = scale value.

S = shunt value.

Table 4.2. Shunt and Scale Values

Shunt No.	Shunt Value (S)	Scale No.	Scale Value (N)
1	1024	1	1
2	512	2	2
3	256	3	4
4	128	4	8
5	64	5	16
6	32	6	32
7	16	7	64
8	8	8	128
9	4		
10	2		
11	1		

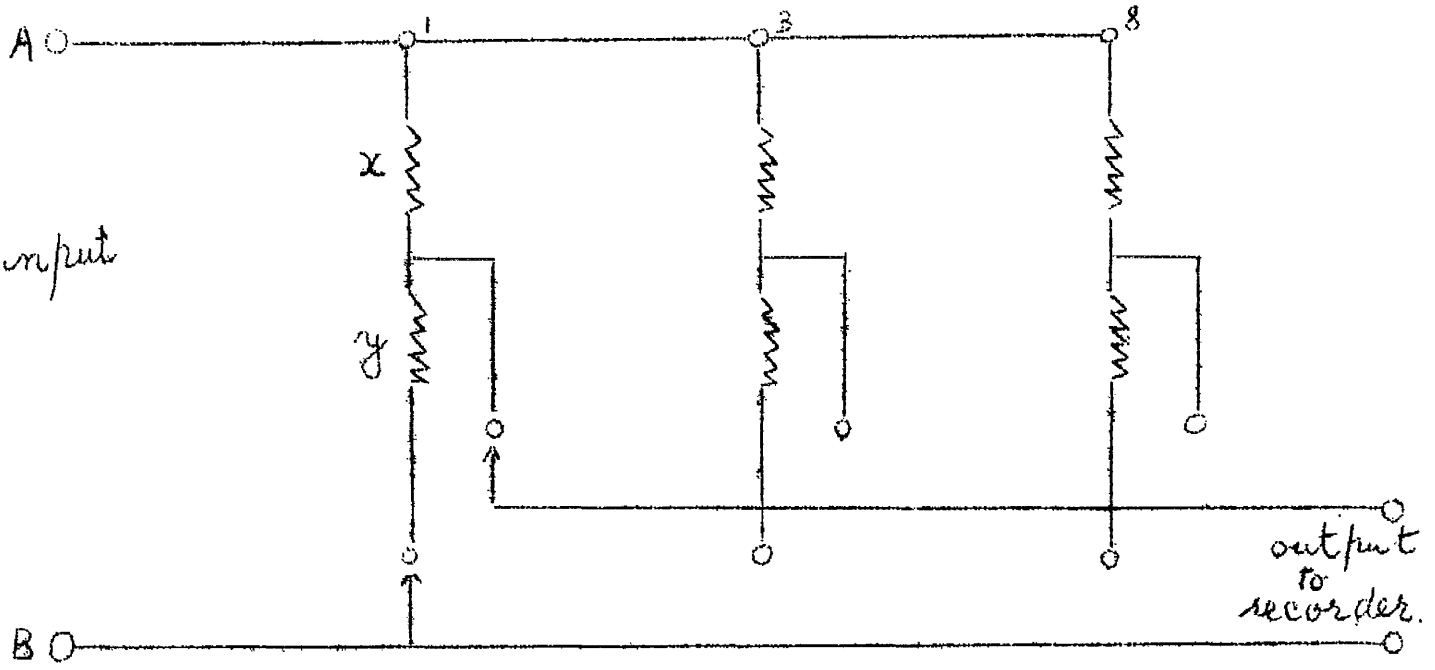
Detailed Description of the Capacitance Cell Circuit

The electrical circuit is shown in Figs. 10, 11.

During the positive half cycle the oscillator is positive to earth. The positive current passes through the balancing cell, is allowed through the germanium diode and goes to earth via the 10KΩ resistance and the recorder. During the negative half cycle the oscillator is negative to earth. The negative current passes through the detecting cell, is allowed through the rectifier, and goes to earth via the decade resistance and the recorder.

The net current, which is the algebraic sum of the two above mentioned currents, generates a voltage across the recorder shunt which appears as a deflection on the recorder chart. The system of shunts across the recorder is of interest and will be described below.

Fig. 11



In order not to affect the external circuit the resistance shown to the external circuit (i.e. the resistance between terminals A and B) had to remain constant. Thus the sum of the resistance (x + y) was always constant but by a switch the relative values of x and y could be altered. Only 3 switch positions are shown on Fig. 11. There were, in fact, 8 positions. The actual values of resistances x and y are given in Table 4.3.

Table 4.3

Scale Number	x	y
8	1990	10
7	1980	20
6	1960	40
5	1920	80
4	1840	160
3	1680	320
2	1360	640
1	720	1280

The whole point of the capacitance cell was that the capacitance of the detecting element should change only when the concentration of potassium chloride flowing through it, changed. Effective capacitance changes due to any other causes had to be eliminated.

This was accomplished as shown below.

Let C = capacitance of tube and solution combined.

and let X_c = impedance of the capacitance.

then $X_c = \frac{1}{2\pi f C}$

where f = frequency.

I.r.m.s., the root mean square current depends on the impedance as shown by equation (6).

$$\text{I.r.m.s.,} = \frac{V}{X_c} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

where V = applied voltage

X_c = effective impedance of circuit.

V comes from a stabilised power supply and is constant.
Therefore I.r.m.s. will be constant provided X_c is constant
X_c will remain constant provided f is constant.

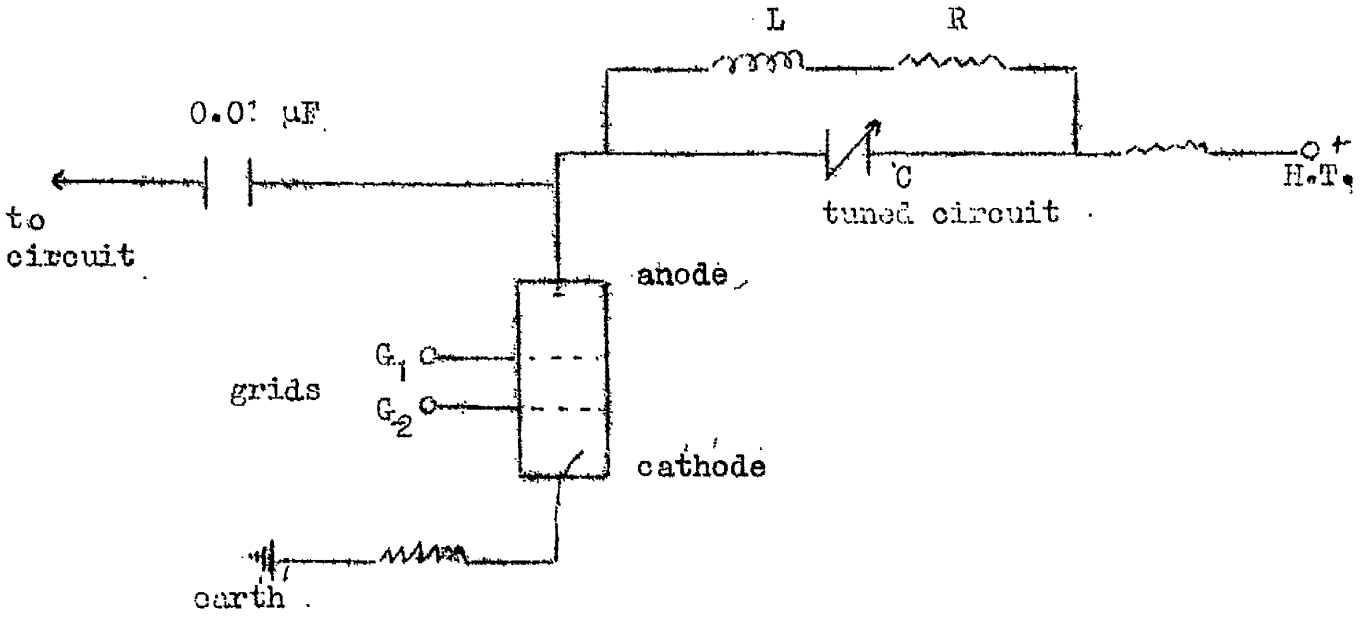
The frequency of oscillation was kept constant by two means:-

(1) A piezoelectric quartz crystal in the grid circuit of the beam tetrode oscillator valve oscillated at its natural frequency of 465 Kc/S, causing the grid voltage to oscillate in resonance.

(2) The high tension voltage supply was kept constant.

A simplified circuit of the oscillator is shown below:

Fig. 12. Oscillator Circuit



Now C = QV ..... (8)

Where Q = the quantity of electricity passed.

V = voltage.

Q is a function of the dielectric which for one substance (e.g. potassium chloride) only changes when the concentration changes.

V is constant since we have a stabilised power supply.

Thus f and V are constant and so C and hence X_c will only change when there is a concentration change in the capacitance cell.

4.1.6.3. Measurement of Desorption using the Conductivity Cell

Several experiments were carried out, in which the concentration of potassium chloride was continuously measured by a recorder coupled to a Wayne Kerr conductivity cell. These experiments were done in connection with the programme outlined in this thesis but were not carried out by this author and brief mention is made for comparison purposes only. The porous cylinder was suspended in a large beaker of water, which was

continuously stirred, and the increasing conductivity continuously measured. A modified solution of the diffusion equation was used to obtain the values of the mutual diffusivity D, which are given in 6.1.1.4.

It should be noted that this is not a flow system.

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5. CALCULATION OF INTEGRAL DIFFUSIVITY FROM THE EXPERIMENTAL DATA

The calculations may be conveniently considered in four sections:-

5.1. Modification of the Theoretical Equation to the form suitable for interpreting the experimental data.

5.2. Calculation of M_o, the mass of solute initially present in the porous cylinder and M_∞, the mass of solute absorbed by the porous cylinder after infinite time.

5.3. Calculation of the integral diffusivities from the theoretical and experimental plots.

5.4. Determination of the Physical Characteristics of the Porous Media.

5.4.1. Pore volume, bulk volume and porosity.

5.4.2. Pore size distribution.

As described in Chapter 4, two methods of experimentally measuring the mutual diffusivity were used. For this reason, sections 5.1 and 5.3 are subdivided according to the experimental method used.

The sections will be discussed in detail below.

5.1. Modification of the Theoretical Equation to a form Suitable for Interpretation

The solutions to Fick's Second Law, for a semi-infinite cylinder and the conditions stated in Chapter 3, are:-

$$\frac{M}{M_o} = 4 \sum_{S=1}^{\infty} \frac{1}{\alpha s^2} \exp. \frac{-Dt \alpha s^2}{c^2} \qquad \ldots\ldots\ldots (26)$$

and, for short times,

$$\frac{M_t}{M_o} = \frac{4}{\pi^{\frac{1}{2}}} \left(\frac{D}{a^2}\right)^{\frac{1}{2}} t^{\frac{1}{2}} - \left(\frac{D}{a^2}\right) t - \frac{1}{3\pi^{\frac{1}{2}}} \left(\frac{D}{a^2}\right)^{3/2} t^{\frac{2}{3}} \quad \ldots\ldots (27)$$

Equations (27) and, to a lesser degree, (26) were used in modified form to determine D, the mutual diffusivity.

D was calculated by two methods:-

(1) The integral method and
(2) The differential method

The integral method was used to determine D from both recording balance and capacitance cell measurements. The differential method was used only to process results from the capacitance cell.

The two methods will be explained in detail below.

Integral Method

A factor which limits both the recording balance and the capacitance cell measurements is that no accurate measurements at time, t=0, and for a short period afterwards, are possible.

Using the recording balance, the weight of the suspended cylinder and its contents cannot be measured at t=0, the time when the liquid stream touches the cylinder, and the first accurate reading is usually noted after two or three minutes. Using the capacitance cell, the concentration downstream cannot be read at t=0, the time when the recorder gives a "kick", as the reading went "off-scale" and the scales and shunts had to be adjusted to give an "on-scale" reading. The first accurate reading is usually noted after two or three minutes.

Thus no absolute measurement of the amount of solute which has entered or left the cylinder between t=0 and t=t can be made.

Instead ΔM, the difference between the mass of solute in the cylinder at two different times, t_1 and t_2 was measured directly and substituted into equation (27) to give:-

$$\frac{\Delta M}{M_o} = \frac{4}{\pi^{\frac{1}{2}}} \left(\frac{D}{a^2}\right)^{\frac{1}{2}} \left(t_1^{\frac{1}{2}} - t_2^{\frac{1}{2}}\right) - \left(\frac{D}{a^2}\right) (t_1 - t_2) - \frac{1}{3\pi^{\frac{1}{2}}} \left(\frac{D}{a^2}\right)^{3/2} \left(t_1^{3/2} - t_2^{3/2}\right) \quad \ldots\ldots (27a)$$

The values of t_1 and t_2 were chosen to give a constant fractional extraction value $\left(\frac{M_t}{M_o}\right)$. Thus the values of t_1 and t_2 varied with the square of the cylinder radius (a). All the short time values were for 0.756 and 0.610 fractional extraction.

A graph of $\frac{\Delta M}{M_o}$ against K, $\left[K = \left(\frac{D}{a^2}\right)^{\frac{1}{2}}\right]$ was drawn with the times t_1 and t_2 as parameter. This will be referred to as the "Solution of the Diffusion Equation for short times" (Fig. 13).

Similarly equation (26) was modified to give:-

$$\frac{\Delta M}{M_o} = 4 \sum_{S=1}^{\infty} \frac{1}{\alpha_s^2} \exp. \left[- \frac{D \alpha_s^2}{a^2} (t_i - t_2 \right] \quad \ldots\ldots\ldots\ldots (26a)$$

The right hand side of equation (26a) was tabulated and summed for values of t_1 and t_2 such that constant values of the fractional extraction of 0.586 and 0.509 were obtained.

A graph of $\frac{\Delta M}{M_o}$ against $\frac{D}{a^2}$ was drawn with the times t_1 and t_2 as parameter. This will be referred to as the "Solution of the Diffusion Equation for long times" (Fig. 14).

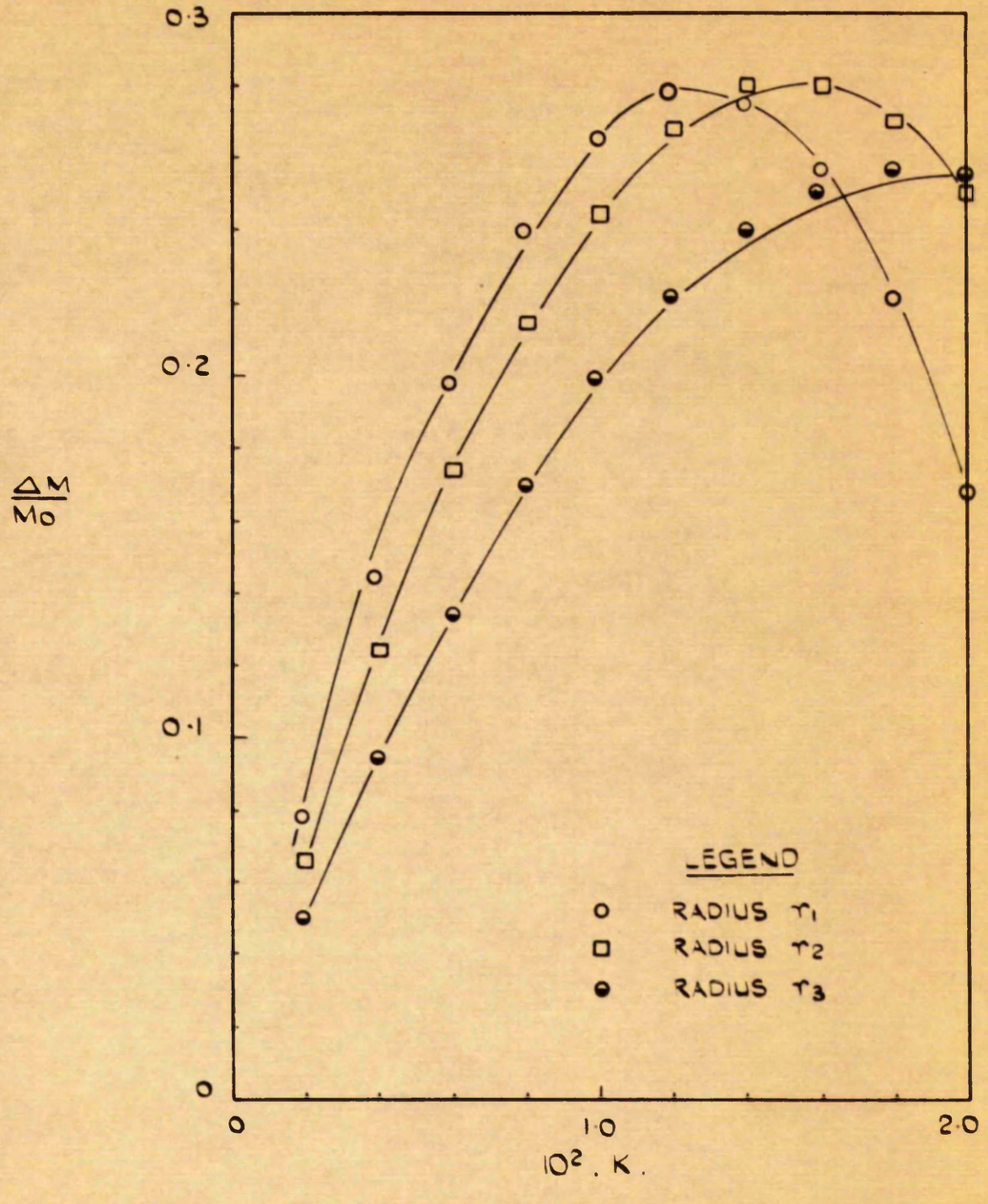
5.2. Calculation of M_o and M_∞

Calculation of M_o, the mass of solute initially in the porous cylinder at the start of a desorption experiment.

W_i, the grams of solution at temperature T_i, and G, the solute concentration in gm/ml. of solution at 20°C., were determined experimentally

$$\frac{W_i}{P_i} = \text{volume of solution at } T_i\,^{\circ}C.$$

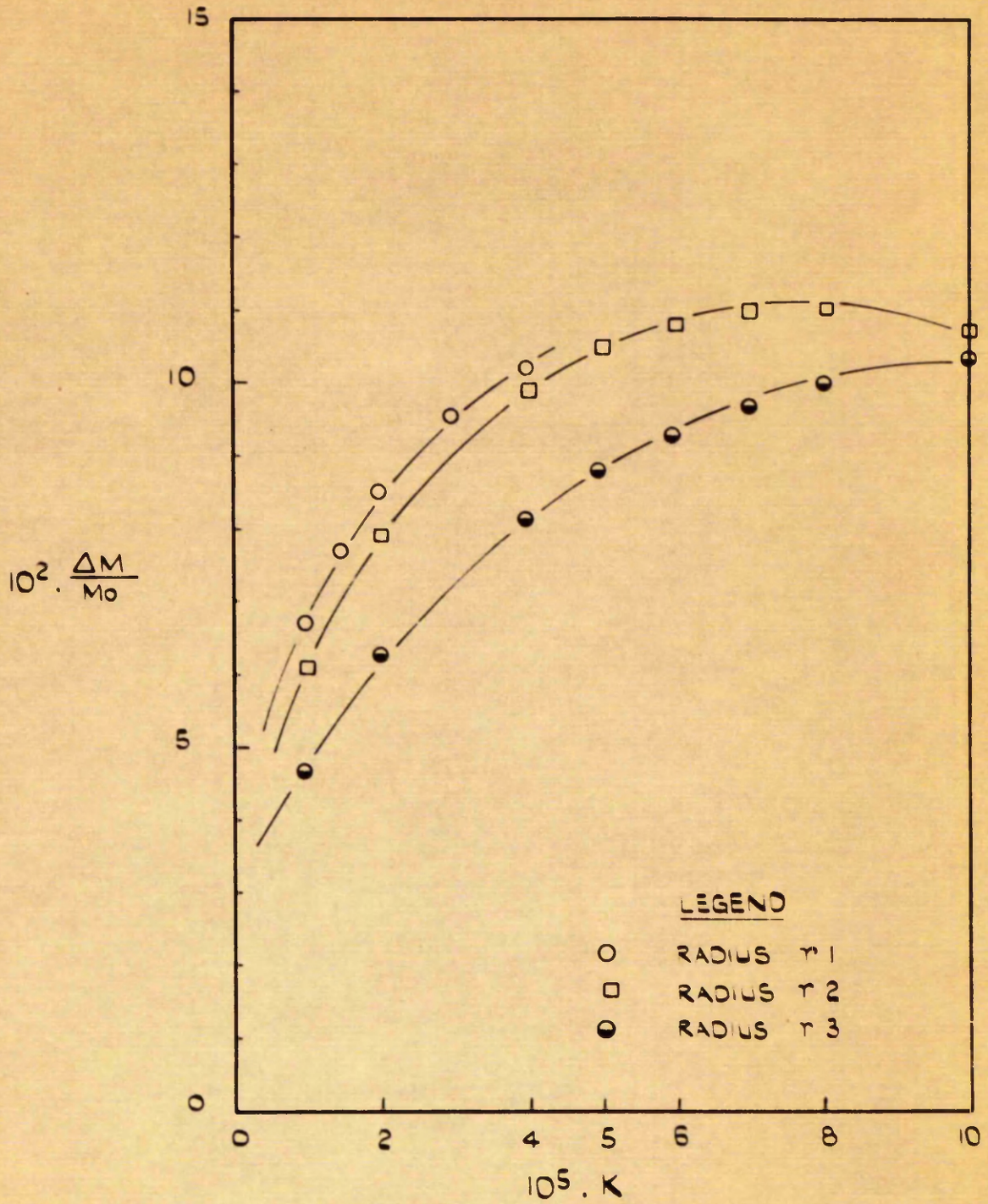
SOLUTION OF THE DIFFUSION EQUATION FOR SHORT TIMES



$\left[K = \left(\frac{D}{a^2}\right)^{1/2} \ (sec^{-1/2}) \ ; \ D \ (cm^2 \ sec^{-1}) \right]$

FIG 13.

SOLUTION OF THE DIFFUSION EQUATION FOR LONG TIMES.



$\left[K = \frac{D}{a^2} (sec^{-1}) ; \quad D (cm^2 sec^{-1}) \right]$

FIG. 14.

where p_i = density of solution at impregnation temperature Ti°C.

Volume of solution at 20°C. = (Volume at Ti) x $\frac{p_i}{p_{20}}$

$$\therefore \quad M_o = \frac{W_i}{p_i} \times \frac{p_i}{p_{20}} \times G$$

$$\therefore \quad M_o = \frac{W_i \times G}{p_{20}} = W_i \times X \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where X = weight fraction of solute.

The determination of X has been described in 4.2.3. and thus M_o can be completely determined.

Calculation of M_∞, the mass of solute which would enter the porous cylinder after infinite time, in an absorption experiment.

Wi, the grams of impregnated pure solvent, and either G, the solute concentration in gm/ml. at 20°C. or X, the solute weight fraction were measured experimentally.

Let p_i^w = density of solvent at impregnation temperature Ti.

p_s^a = density of the circulating solution at the absorption temperature.

p_s^{20} = density of the circulating solution at 20°C.

The occupied pore volume = $\frac{W_i}{\rho_i^w}$

This volume, at infinite time, would be occupied by solution at T_a, the absorption temperature.

$$\therefore \quad \text{Mass of solution at infinite time} = \frac{W_i \times p_s^a}{p}$$

$$\therefore \quad M_\infty = \frac{W_i \times p_s^a \times G}{p_i^w \times p_s^{20}} = \frac{W_i \times X \times p_s^a}{p_i^w} \qquad \ldots\ldots\ldots\ldots (2)$$

5.3. Calculation of the Integral Diffusivity from the Theoretical and Experimental Plots

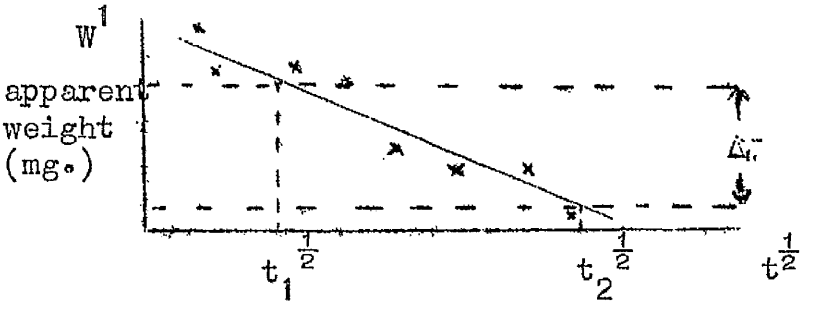
5.3.1 Calculation using the Experimental Results from the Recording Balance Method

From the recorder chart, tables of the apparent weight of cylinder and contents against time and the square root of time were drawn up.

For the short time calculation, a graph of apparent weight (in mg.) against $t^{\frac{1}{2}}$ was drawn. For the long time calculation a graph of apparent weight against t was drawn.

Short Time Calculation:

From the experimental graph, which was always a straight line or very nearly so,



ΔW, the apparent weight change in the time interval $(t_1 - t_2)$ was read off.

Derivation of ΔM from ΔW

As solute enters or leaves the porous cylinder, solvent leaves or enters. Thus ΔM, the mass of solute entering or leaving in the time interval $(t_1 - t_2)$ will always be greater than ΔW, the net weight change of the porous cylinder.

The determination of ΔM is given below:

Let ΔW = apparent weight change between t_1 and t_2.

V = pore volume of the cylinder.

$\bar{p}_1$ = mean density of the solution in the cylinder at t_1.

$\bar{p}_2$ = mean density of the solution in the cylinder at t_2.

$$\therefore \quad \Delta W = V(\bar{p}_1 - \bar{p}_2)$$

Now, $\bar{p}_t$, mean density of the solution in the cylinder at any time t is defined as:

$$\bar{p}_t = \frac{2}{a^2} \int_0^a p_t \, r \, d \, r$$

where r = general radius of cylinder

a = outer radius of cylinder

p_t = density of solution at any point within the cylinder.

The following assumption is now made:

$$p_t = p_w + k \, C_t$$

where p_w = density of pure solvent

k = a constant

C_t = concentration of solution at any time, i.e. it is assumed that there is a linear relationship between the density of the solution and the solute concentration.

$$\therefore \Delta W = V \frac{2}{a^2} \int_0^a (p_w + k \, C_t) \, r \, dr \Big|_{t_1}^{t_2}$$

$$= V p_w + \frac{2 Vk}{a^2} \int_0^a C_t \, r \, dr \Big|_{t_1}^{t_2}$$

$$= V p_w + \frac{4 V k Co}{a^2} \sum_{n=1}^{\infty} \frac{1}{x_n^2} \cdot e^{- D x_n^2 t} \Big|_{t_1}^{t_2}$$

Putting $x_n = \frac{\alpha_n}{a}$

$$\therefore \Delta W = V p_w + 4 Vk Co \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} e^{- \frac{D \alpha_n^2}{a^2} t} \Big|_{t_1}^{t_2}$$

Now $V Co = Mo$ and from equation (26a)

$$4 \sum_{n=1}^{\infty} \frac{1}{\alpha_n^2} e^{- D \frac{\alpha_n^2 t}{a^2}} = \frac{\Delta M}{Mo}$$

$$\therefore \Delta W = Mo \cdot k \cdot \frac{\Delta M}{Mo}$$

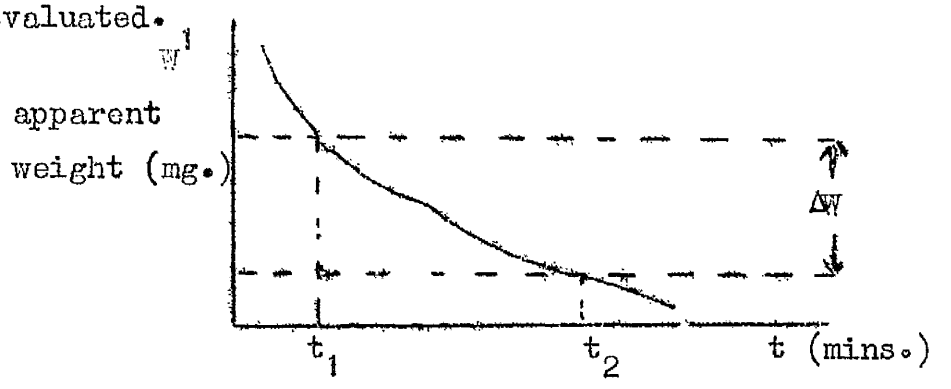
$$\therefore \Delta M = \frac{1}{k} \Delta W$$

Graphs of density against solute concentration at 25°C, the sorption temperature, were drawn. In all cases a straight line resulted and thus the assumption was justified.

ΔM was thus available, Mo was obtained as shown in 5.2. and from the value of $\frac{\Delta M}{Mo}$, the value of K was read off "The Solution of the Diffusion Equation for short times" (Fig. 13). From a knowledge of the exact radius (a) of the cylinder being used, the integral diffusivity D could then be evaluated.

Long Time Calculation:

From the experimental graph, ΔW was read off. ΔM was calculated from ΔW by the method used in the short time calculation.



With the value of $\frac{\Delta M}{Mo}$ known, the value of D/a^2 was read off the "Solution of Diffusion Equation for Long Times" (Fig. 14). From a knowledge of the exact radius (a) of the cylinder being used, the integral diffusivity D was evaluated.

5.3.2. Calculations using the Experimental Results from the Capacitance Cell Method

The short time calculation was found more accurate and convenient than the long time calculation. It was therefore decided to use only the short time calculation.

Two methods of using the short time calculation were worked out and will be considered in detail below. They are:

(1) The integral method, and,

(2) The differential method.

Calculation of D by the Integral Method

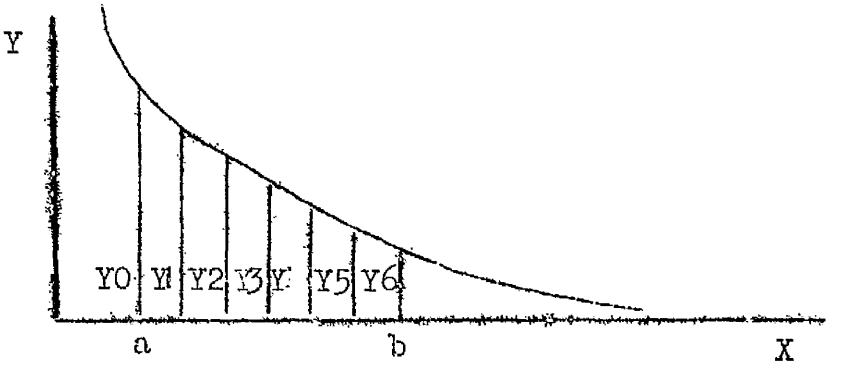
Two terms of the integral solution to Fick's Second Law were used to calculate D, the integral diffusivity. The form used was:-

$$\frac{\Delta M}{Mo} = \frac{4}{\pi^{\frac{1}{2}}} \left(\frac{D}{a^2}\right)^{\frac{1}{2}} \left(t_2^{\frac{1}{2}} - t_1^{\frac{1}{2}}\right) - \left(\frac{D}{a^2}\right) (t_2 - t_1) \quad \ldots\ldots (10)$$

The experimental values of $\frac{dm}{dt}$ were plotted against time. Graphical integration between the limits, t_1 and t_2 yielded the value of ΔM which was then substituted into equation (10) which was solved and D evaluated. The limits of integration chosen were t_1 = 5 minutes and t_2 = 35 minutes.

The graphical integration was carried out using the Weddle rule. This method involves dividing the area into six equal strips and measuring the lengths of the ordinates Y0, Y1 ..... Y6. (See Fig. 16).

The area under the curve can then be calculated from the formula:-



$$I = \frac{b - a}{20} [Y0 + 5Y1 + Y2 + 6Y3 + Y4 + 5Y5 + Y6]$$

where a and b are the limits of integration.

Calculation of D by the Differential Method

The differential form of the solution to Fick's Second Law for short times is:-

$$\frac{dm}{dt} = \frac{2\,Mo}{\pi^{\frac{1}{2}}} \left(\frac{D}{a^2}\right) t^{-\frac{1}{2}} - \frac{D\,Mo}{a^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Thus a plot of $\frac{dm}{dt}$ against $t^{-\frac{1}{2}}$ should give a straight line of slope $\frac{2\,Mo}{\pi^{\frac{1}{2}}}\left(\frac{D}{a^2}\right)^{\frac{1}{2}}$ and intercept $\left(\frac{-\,D\,Mo}{a^2}\right)$ on the $\frac{dm}{dt}$ axis. It should thus be possible to calculate D from both the intercept and the slope. In practice, however, it was found that a straight line resulted but the intercept was too small to enable D to be calculated accurately and only the slope was used. The slope of the straight line giving the best fit to the experimental points was found by the method of least squares.

Specimen calculations by the different methods are given below.

5.3.1. Specimen Calculation using Short and Long Time Calculations for Results obtained using the Recording Balance

Tables from the Recording Balance Chart

	$t^{\frac{1}{2}}$(min.$^{\frac{1}{2}}$)	t(min.)	Wa apparent wt (gm.)	W^1 = (Wa - 13.00) mg
Short Time Results	2.83	8	13.0280	28
	3.16	10	13.0400	40
	3.61	13	.0550	55
	4.00	16	.0684	68.4
	4.24	18	.0761	76.1
	4.47	22	.0839	83.9
	4.90	24	.0973	97.3
	5.20	27	.1065	106.5
	5.29	28	.1095	109.5
	5.48	30	.1148	114.8
Long Time Results		34	.1255	125.5
		38	.1355	135.5
		42	.1452	145.2
		46	.1542	154.2
		48	.1580	158.0
		52	.1656	165.6
		54	.1691	169.1
		56	.1736	173.6
		62	.1840	184.0
		64	.1867	186.7
		70	.1962	196.2
		72	.1993	199.3
		76	.2054	205.4
		78	.2079	207.9
		82	.2141	214.1
		84	.2161	216.1
		90	.2240	224.0
		92	.2262	226.2
		94	.2284	228.4
		100	13.2354	235.4

Run No. 17.3. Solute Potassium Chloride Normality 3N

Cylinder No.	$(\text{Radius})^2$ $(\text{cm})^2$	Wt. of Cyl. + Tin (gm.)	Dry Wt. of Cyl. (gm.)	Wt. of Tin, Cyl. + Solute (gm.)	Wt. of Solution (gm.)
3	0.443	25.9314	15.6642	29.4651	3.5336
Wt. of Tin		(1) 10.2672		(2) 10.2673	

Mean titre of standard silver nitrate	13.70 ml.
Normality of circulating solution (absorption)	2.728
Weight fraction of solute, X	0.1814
M_∞, mass solute in cylinder after infinite time	0.7174 gm.
Weight in recording balance pan	13.00 gm.
Pressure Difference (cm. mercury)	Initial 14.0
	Final 14.1
Mass Flowrate (kg./min.)	0.26
Radius of annulus (cm.)	0.4
Re, Reynold's No. in the annulus	700
Impregnation Pressure (mm. mercury)	0.02
Impregnation temperature ($^\circ$C.)	21°C.
Stream Temperature Td	Initial 25.0°C.
	Final 25.0°C.
Water Bath Temperature	Initial 26.8°C.
	Final 26.8°C.
1/k	1.672

Short Time Solution for $t_1^{\frac{1}{2}} = 3$ min.$^{\frac{1}{2}}$; $t_2^{\frac{1}{2}} = 5$ min.$^{\frac{1}{2}}$.

ΔW (mg.)	64.6	$k^2 = \frac{D}{a^2}$	2.46×10^{-5}
$\frac{\Delta M}{M_\infty}$	0.1505	Factor (a^2)	0.443
K	0.00496	D ($\text{cm}^2/\text{sec.}$)	1.09×10^{-5}

Long Time Solution for t_1 = 28 min; t_2 = 43 min.

ΔW (mg.)	30.3	$\frac{D}{a^2}$	2.46×10^{-5}
$\frac{\Delta M}{M_\infty}$	0.0706	Factor D (cm^2/sec.)	0.443 1.09×10^{-5}

5.3.2. Specimen Calculation for Capacitance Cell Results

Run B7 (see Fig. 16)

Experimental Data and Derived Quantities for a Typical Run using the Capacitance Cell

Cylinder No. M5
Container No. 7

Cylinder radius = 0.6459 cm
$(\text{cylinder radius})^2 = 0.4172\ cm.^2$

Weight of Dry Cylinder + container = 29.2789 g.
Weight of Empty Container = 10.2952 g.
Weight of Dry Cylinder = 18.9837 g.
Weight of Impregnated Cylinder + Container = 35.1174 g.
Weight of Empty Container = 10.3349 g.
Weight of Impregnated Cylinder = 24.7825 g.
Weight of Solution = 5.7988 g.
Concentration of Impregnating Solution = 3.195 N
Weight per cent of K Cl in solution = 20.94%

$\therefore$ Mo = 5.7988 x 0.2094 x 1000
= 1214 mg.

Manometer reading = 16.3 cm. Hg.

$\therefore$ Flowrate = 0.207 kg./min.

(1) Integral Method

$$\Delta M = \frac{35-5}{20}\left[22.0 + (5 \times 15.3) + 12.5 + (6 \times 10.4) + 8.9 + (5 \times 7.8) + 7.0\right]$$
$$= 342.5 \text{ mg.} \quad \text{(By the Weddle Rule)}$$

For t_1 = 5 min. and t_2 = 35 min.

$$\frac{\Delta M}{Mo} = \frac{4}{\pi^{\frac{1}{2}}}\left(\frac{D}{a^2}\right)^{\frac{1}{2}}(5.916 - 2.236) - \left(\frac{D}{a^2}\right)(35-5)$$

$$\therefore 30\left(\frac{D}{a^2}\right) - 8.307\left(\frac{D}{a^2}\right)^{\frac{1}{2}} + \frac{\Delta M}{Mo} = 0$$

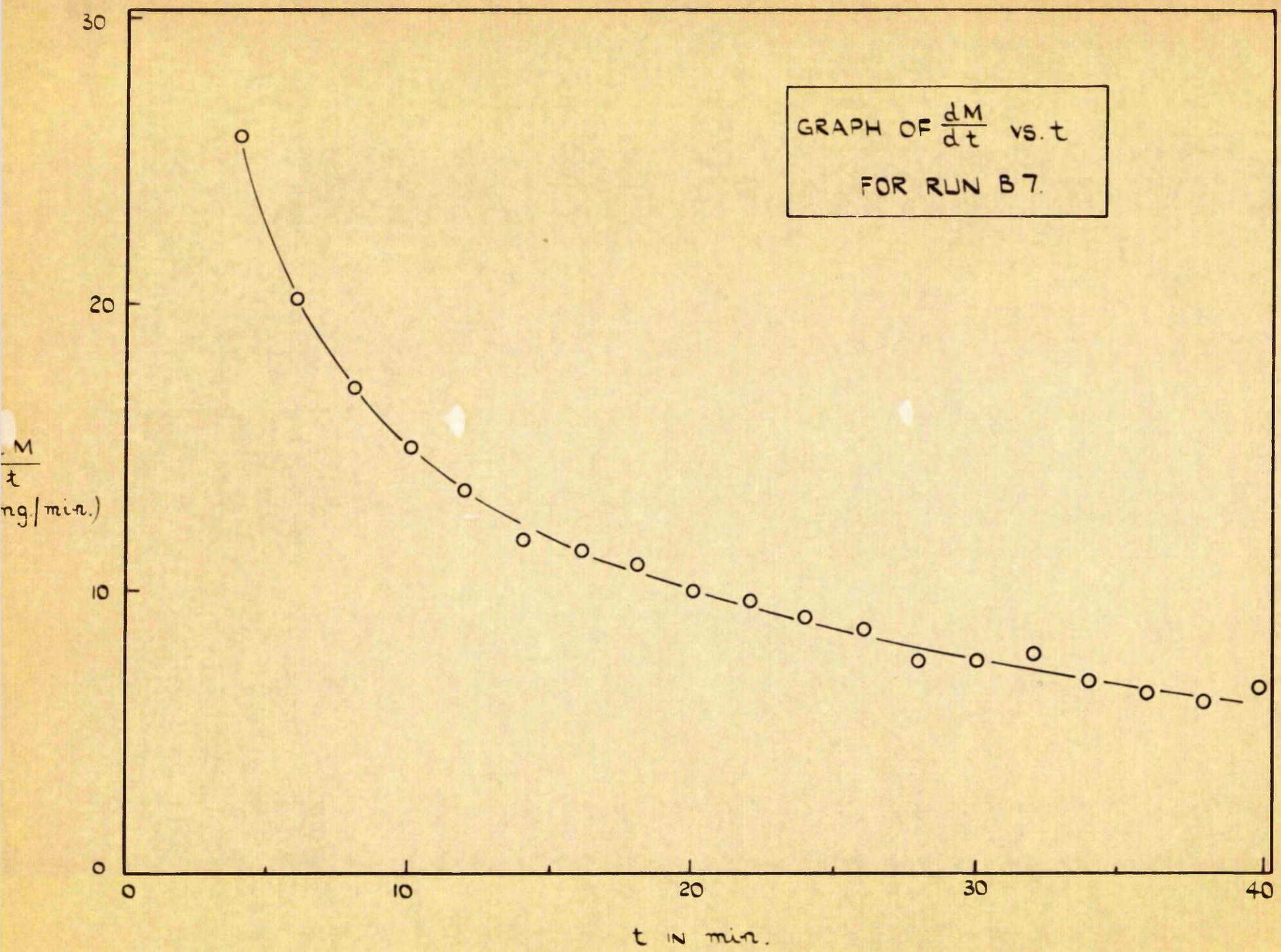

GRAPH OF $\frac{dM}{dt}$ vs. t
FOR RUN B 7.
30
20
10
0
0
10
20
30
40
t IN min.
$\frac{\Delta M}{\Delta t}$
ng./min.)

FIG 16.

$$\therefore \quad \left(\frac{D}{a^2}\right)^{\frac{1}{2}} = \frac{8.307 \pm \sqrt{[69.01 - 120\,\frac{\Delta M}{Mo}]}}{60}$$

Substituting $\Delta M = 342.5$ mg. and $Mo = 1214$ mg.

Neglecting the nonsensical value,

$$\therefore \quad \left(\frac{D}{a^2}\right)^{\frac{1}{2}} = 0.03962$$

$$\therefore \quad D = (3.962)^2 \times 10^{-4} \times 0.4172 \text{ cm.}^2/\text{min.}$$

$$D = 1.12 \times 10^{-5} \text{ cm.}^2/\text{sec.}$$

(2) Differential Method

Table Least Squares Calculation for Run B7

t	$t^{-\frac{1}{2}}$	$\frac{dm}{dt}$	t^{-1}	$t^{-\frac{1}{2}} \times \frac{dm}{dt}$
min.	$\text{min.}^{-\frac{1}{2}}$	mg/min.	min^{-1}	$\text{mg.min.}^{-3/2}$
10	0.3162	14.9	0.10000	4.71138
12	0.2887	13.5	0.08333	3.89745
14	0.2673	11.8	0.07143	3.15414
16	0.2500	11.4	0.06250	2.85000
18	0.2356	11.0	0.05556	2.59160
20	0.2236	10.0	0.05000	2.23600
22	0.2132	9.7	0.04545	2.06804
24	0.2041	9.2	0.04167	1.87772
26	0.1964	8.8	0.03846	1.72832
28	0.1889	7.7	0.03571	1.45453
30	0.1826	7.7	0.03333	1.40602
32	0.1768	8.0	0.03125	1.41440
34	0.1715	7.0	0.02941	1.20050
36	0.1667	6.6	0.02778	1.10022
38	0.1622	6.3	0.02632	1.02186
40	0.1581	6.8	0.02500	1.07508
Totals	3.4019	150.4	0.7572	33.78726

$$\therefore \quad \text{Slope} = \frac{16 \times 33.78726 - 3.4019 \times 150.4}{16 \times 0.7572 - (3.4019)^2}$$

$$= 53.384473$$

$$\therefore \quad \left(\frac{D}{a^2}\right)^{\frac{1}{2}} = \frac{0.886}{1214} \times 53.384473$$

$$= 0.0389609$$

$$\therefore \quad D = (3.89609)^2 \times 10^{-4} \times 0.4112 \text{ cm./min.}$$

$$= 1.55543 \times 10^{-5} \text{ cm}^2/\text{sec.}$$

$$\therefore \quad D = 1.06 \times 10^{-5} \text{ cm}^2/\text{sec.}$$

5.4. Determination of the Physical Characteristics of the Porous Media

5.4.1. Pore Volume, Bulk Volume and Porosity

Let Wd = weight of porous cylinder, dry.

Wb = weight of porous cylinder, suspended in water.

Wc = weight of porous cylinder, containing water.

Then, weight of water in cylinder = (Wc - Wd) gm.

Assuming density of impregnating water = 1 gm/c.c.

Total Pore Volume = (Wc - Wd) c.c.

By Archimedes,

Bulk volume = (Wc - Wb) c.c.

and $\text{Porosity} = \frac{\text{Total Pore volume}}{\text{Bulk volume}} \times 100$

The bulk or geometrical volume of the cylinder can also be obtained by measurement of the cylinder length and radius.

5.4.2. Pore Entry Size Distribution

The pressure required to force mercury through a pore is related to pore radius according to the Ritter and Drake equation:

$$r = \frac{-2\sigma \cos\theta}{p}$$

where r = pore entry radius in microns (μ)

σ = surface tension of mercury in dynes/cm.

θ = angle of contact between mercury and the specimen

p = applied pressure in dynes/cm.^{2}

Substituting the values assumed by Ritter and Drake for σ (480 dynes/cm.) and θ (140°) and altering the units, this reduces to

$$d = \frac{215}{P}$$

where d = pore entry diameter in microns (μ)

and P = applied pressure in lb./sq. in.

The results were plotted as curves of accumulated pore volume (expressed as a percentage of the bulk volume of the specimen) and as pore volume (expressed as a percentage of total pore volume) against pore entrance diameter. The results and graphs are given in section 6.

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6. EXPERIMENTAL RESULTS

INTRODUCTION

The experimental results are presented in three sections:-

(1) Experimental values of D, the integral mutual diffusivity of the system studied. The values of D are presented in such a way that the variation of D with (a) the solute-solvent system and (b) the porous media can be discussed conveniently.

(2) Calculated values of the ratio of the diffusivity in free solution to the diffusivity in the porous media. This ratio has been given the symbol K^2 (see Introduction, Section 1.3.1.).

(3) Calculated values of the experimental diffusivity, D, divided by the fractional porosity of the individual cylinder. This has been denoted by D^1.

The results are examined in detail in subsequent sections.

6.1. Experimental Values of D, the integral mutual diffusivity

6.1.0. Introduction

Series of factorial experiments were carried out with each solute-solvent system and each porous material. The experimental results were analysed for the effects of initial solute concentration, cylinder radius, direction of mass transfer and solvent flowrate. The values of D were calculated by both the "short time" and "long time" calculations in the case of the systems H125 - KCl and H125 - CCl_4. The results are presented in tables together with the conclusions which may be derived from the statistical analyses.

Graphs of D *vs* properties of the solute-solvent systems and properties of the porous media are given in Figs. 17 - 30. A specimen calculation of a statistical analysis is given in Appendix 4.

6.1.1. Results for absorption and desorption using H125 cylinders

6.1.1.1. Short Time Values of D for KCl - water

Table 6.1. Short Time Values of D for KCl - water

No. of Run.	10^6 D(cm^2 $sec.^{-1}$)	10^6 D repeat (cm^2 $sec.^{-1}$)	
r_1 c_1 a	12.0	10.5	
r_1 c_2 a	11.1	10.9	
r_1 c_3 a	11.5	11.9	
r_2 c_1 a	10.9	11.0	
r_2 c_2 a	11.1	11.0	Legend r_1 0.77 cm radius
r_2 c_3 a	10.9	10.7	r_2 0.65 cm radius
r_3 c_1 a	12.1	11.3	r_3 0.52 cm radius
r_3 c_2 a	11.9	13.0	c_1 1N
r_3 c_3 a	11.9	10.9	c_2 2N
r_1 c_1 d	10.9	10.6	c_3 3N
r_1 c_2 d	10.5	11.3	a absorption
r_1 c_3 d	10.4	9.1	d desorption
r_2 c_1 d	11.1	11.0	
r_2 c_2 d	11.1	10.8	$10^6 \bar{D} = (11.30 \pm 0.14)$ cm^2 $sec.^{-1}$
r_2 c_3 d	10.5	9.5	Omitting runs at radius r_3;
r_3 c_1 d	13.0	13.4	$10^6 \bar{D} = (10.80 \pm 0.10)$
r_3 c_2 d	12.3	13.5	cm^2 $sec.^{-1}$
r_3 c_3 d	11.0	12.4	

Experiments were carried out at three initial solute concentrations, three radii, absorption and desorption, with repeats, i.e. a total of thirty six experiments.

Conclusions of statistical analysis:

(1) Radius r, is significant at 0.1% level.

(2) Interaction cm, is almost significant at 5% level.

(3) No appreciable difference between absorption, desorption.

(4) D decreases as C, initial solute concentration, increases.

(5) D decreases as r, cylinder radius, increases.

Separate statistical analyses were carried out for absorption and desorption. The conclusions were:

Absorption only: No factors significant

i.e. D_a = constant

Desorption only: (1) radius r significant at 0.1% level

(2) initial solute concentration, c, significant at 1% level.

i.e. $D_d = f_1 (r) + f_2 (c)$

6.1.1.2. Experimental Values of D, Calculated using solution of the Diffusion Equation for Long Times

The "long time" results, both for K Cl and CCl_4 (carbon tetrachloride), were calculated using equation (26a) (see Section 5.1) in graphical form. In order to obtain values of the fractional extraction of 0.586 and 0.509, the following time intervals were chosen:

r_1 nominal radius 0.77 cm; t_1 = 40, t_2 = 60 min.

r_2 nominal radius 0.65 cm; t_1 = 28, t_2 = 43 min.

r_3 nominal radius 0.52 cm; t_1 = 18, t_2 = 27 min.

Table 6.2. "Long Time" Values of D for K Cl - water

No. of Run.	10^6 D(cm^2 $sec.^{-1}$)	10^6 D Repeat (cm^2 sec^{-1})	Legend
r_1 c_1 a	11.9	10.2	r_1 0.77 cm radius
r_1 c_2 a	14.0	12.2	r_2 0.65 cm radius
r_1 c_3 a	11.4	11.5	r_3 0.52 cm radius
r_2 c_1 a	11.1	11.5	c_1 1N
r_2 c_2 a	11.9	9.7	c_2 2N
r_2 c_3 a	9.2	8.6	c_3 3N
r_3 c_1 a	13.1	12.?	a absorption
r_3 c_2 a	14.1	11.?	d desorption
r_3 c_3 a	14.2	10.9	
r_1 c_1 d	10.6	12.2	
r_1 c_2 d	10.9	12.1	$10^6 \bar{D} = (11.6 \pm 0.3)$ cm^2 sec^{-1}
r_1 c_3 d	10.8	11.1	
r_2 c_1 d	11.9	10.6	
r_2 c_2 d	9.6	11.5	
r_2 c_3 d	9.6	10.8	
r_3 c_1 d	12.6	10.7	
r_3 c_2 d	14.0	15.3	
r_3 c_3 d	11.1	13.0	

Conclusions of Statistical Analysis:

(1) Radius r, is significant at 0.1% level.

(2) Initial solute concentration, c, is almost significant at 5% level.

(3) No appreciable difference between absorption and desorption.

(4) D goes through a maximum at initial solute concentration c_2.

(5) D goes through a minimum at cylinder radius r_2.

Conclusions (2), (4) and (5) differ from those for the "short time" results.

6.1.1.3. Experimental Values of the Integral Mutual Diffusivity Obtained from Desorption Experiments Using the Capacitance Cell

The values of D, the integral mutual diffusivity, determined by the integral and differential methods as described in section 5.3.2., are given in table 6.3.

Table 6.3.

No. of Run	(Cylinder radius)^2 (cm^2)	Flowrate ($kg\ min^{-1}$)	K Cl Concentration gm. equiv/litre	10^5 D ($cm^2\ sec^{-1}$)	
				Integral Method	Differential Method
A1	0.5862	0.226	3	1.30	1.18
A2	0.5873	0.100	3	2.34	4.12
A3	0.5833	0.335	3	1.76	2.60
A4	0.5778	0.284	3	1.19	1.93
B1	0.5862	0.260	3	1.12	1.03
B2	0.5873	0.260	3	1.32	1.47
B3	0.5833	0.260	3	1.20	1.05
B4	0.5778	0.260	3	0.70	0.47
B5	0.4081	0.207	3	1.38	1.27
B6	0.4168	0.207	3	1.07	0.89
B7	0.4172	0.207	3	1.12	1.06
C1	0.5862	0.260	1	1.38	1.41
C2	0.5873	0.260	1	0.97	1.30
C3	0.5833	0.260	1	1.10	1.12
C4	0.5778	0.260	1	1.31	1.33
C5	0.4081	0.207	1	1.54	1.37
C6	0.4168	0.207	1	1.06	1.88
C7	0.4172	0.207	1	1.20	1.61
D1	0.5862	0.160	3	0.56	0.39
D2	0.5873	0.160	3	0.79	0.70
D3	0.5833	0.160	3	0.97	0.92
E1	0.5862	0.329	3	0.81	0.98
E2	0.5873	0.329	3	0.82	0.82
E4	0.5778	0.329	3	0.74	0.79
F1	0.5862	0.166	3	1.16	1.14
F2	0.4081	0.332	3	1.27	1.04

The very large values of the diffusivity obtained in runs A2, A3, A4 and C6 are believed to have been caused by the presence of potassium chloride in the pump, which had previously been used for absorption experiments. The low values of the diffusivity obtained in runs D1, D2, D3, E1, E2 and E4 are believed to have been caused by a fault in the counting mechanism of the recorder integrator.

The very low value of the diffusivity obtained in Run B4 could only be due to incorrect balancing of the electrical circuit.

These specific runs were ignored when the results obtained by this technique were being evaluated.

The mean values of the diffusivity and the standard errors are given below.

Integral Method $(1.23 \pm 0.04) \times 10^{-5}$ cm^2 sec^{-1}

Differential Method $(1.23 \pm 0.05) \times 10^{-5}$ cm^2 sec^{-1}

Since its standard error is slightly smaller, the integral values were taken when considering the significance of initial potassium chloride concentration, flowrate and cylinder radius.

Effect of Initial Potassium Chloride Concentration

The concentration effect is shown in table 6.4.

Table 6.4.

Initial K Cl Concentration (gm. equiv./litre)	10^5 Mean Value of D. (cm^2 sec^{-1})	10^5 Standard Error (cm^2 sec^{-1})
1N	1.25	0.08
3N	1.22	0.04

Effect of Flowrate and Cylinder Radius

The values from series B and C were used to evaluate the effect of flowrate and cylinder radius.

The effect of radius alone or flowrate alone cannot be determined from the available experimental results.

Table 6.5

Flowrate (kg/min)	Cylinder Radius (cm)	10^5 Mean Value of D ($cm^2\ sec^{-1}$)	10^5 Standard Error ($cm^2\ sec^{-1}$)
0.207	0.64	1.23	0.08
0.260	0.76	1.20	0.06

The values of K^2 for H125 are given in table 6.6.

Table 6.6

K Cl Initial Concentration (gm. equiv./litre)	K^2
1N	1.50
3N	1.73

6.1.1.4. Experimental Values of the Integral Mutual Diffusivity obtained from Desorption Experiments using the Conductivity Cell

D, the mutual diffusivity of K Cl in water, was experimentally determined by Dr. MacDonald using a continuously recording conductivity cell. This work was carried out towards the end of the present research and the available results are included here for comparison purposes.

The values of D, the integral mutual diffusivity of KCl-water for H125 cylinders, calculated by the solution of Fick's Law for long times, are given below.

The weight fraction of the impregnating solution was 0.1917 in all cases, i.e. the initial solute concentration was approximately 3N.

Cylinder Number	Radius Group	10^5 D (cm^2 sec^{-1})	10^5 D Repeat (cm^2 sec^{-1})
5	4	1.05	
3	4	1.07	
6	4	1.04	
1	2	0.99	
2	2	1.03	
4	2	1.00	0.96
1	3	1.20	
4	3	1.20	
15	3	1.27	
10	3	1.13	
11	3	1.18	

$10^5 \bar{D} = (1.02 \pm 0.014)$ (radius groups 2 and 4)

$10^5 \bar{D} = (1.20 \pm 0.025)$ (radius group 3)

Table 6.7. Short Time Values of D for Sucrose-Water

No. of Run	$10^6 D$ (cm^2 sec^{-1})	Legend
r_1 c_1 a	2.79	
r_1 c_2 a	2.66	r_1 0.77 cm, radius
r_2 c_1 a	2.84	r_2 0.65 cm, radius
r_2 c_2 a	2.93	r_3 0.52 cm, radius
r_3 c_1 a	3.06	c_1 15 weight %
r_3 c_2 a	2.72	c_2 30 weight %
r_1 c_1 d	2.66	-------
r_1 c_2 d	2.59	
r_2 c_1 d	2.74	$10^6 \bar{D} = (2.79 \pm 0.04)$ cm^2 sec^{-1}
r_2 c_2 d	2.63	
r_3 c_1 d	3.06	
r_3 c_2 d	2.74	

Experiments were carried out at two initial solute concentrations, three cylinder radii, absorption and desorption, without repeats, i.e. a total of twelve experiments.

Conclusions of statistical analysis:

(1) All factors are insignificant at 5% level.

(2) Initial solute concentration c, is almost significant at 5% level.

(3) Absorption occurs more quicly than desorption.

(4) D decreases as c, increases.

(5) D decreases as r, cylinder radius, increases.

Table 6.8. "Short Time" Values of D for Carbon Tetrachloride-Methanol

No. of Run	10^6 D (cm^2 sec^{-1})	10^6 D repeat (cm^2 sec^{-1})	Legend
r_1 c_1 a	10.0	9.9	
r_1 c_2 a	10.2	10.2	r_1 0.77 cm. radius
r_1 c_3 a	8.6	8.9	r_2 0.65 cm. radius
r_2 c_1 a	10.0	10.8	r_3 0.52 cm, radius
r_2 c_2 a	9.8	8.7	c_1 40 weight %
r_2 c_3 a	8.7	8.5	c_2 50 weight %
r_3 c_1 a	10.7	10.0	c_3 60 weight %
r_3 c_2 a	9.3	10.1	
r_3 c_3 a	8.9	8.5	
r_1 c_1 d	10.2	10.2	$10^6 \bar{D} = (9.77 \pm 0.08)$ cm^2 sec^{-1}
r_1 c_2 d	11.0	10.6	
r_1 c_3 d	10.2	10.1	
r_2 c_1 d	10.0	10.3	
r_2 c_2 d	9.8	9.7	
r_2 c_3 d	8.6	8.8	
r_3 c_1 d	10.6	10.4	
r_3 c_2 d	10.3	9.9	
r_3 c_3 d	9.8	9.5	

Experiments were carried out at three initial solute concentrations, three cylinder radii, absorption and desorption, with repeats, i.e. a total of thirty six experiments.

Conclusions of Statistical Analysis

(1) Interactions cm and cr are significant at 5% level.

$$\therefore D = f_1 (cm) + f_2 (cr)$$

(2) D decreases as c increases.

(3) Desorption occurs more quickly than absorption.

(4) D goes through a minimum at cylinder radius, r_2.

Since inspection of the results indicated that the values of D at radius r_1 were anomalous, a statistical analysis of the results using only cylinders, of radius r_2 and r_3 was carried out. The conclusions are:-

(1) No interaction is significant at the 5% level.
(2) Initial solute concentration, c, is significant at 0.1% level.
(3) Radius, r, is significant at 5% level.
(4) D decreases as c increases.
(5) Desorption occurs more quickly than absorption.
(6) D decreases as r increases.

6.1.1.4. Table 6.9. "Long Time" Values of D for Carbon Tetrachloride-Methanol

No. of Run	10^6 D (cm^2 sec^{-1})	10^6 D repeat (cm^2 sec^{-1})	Legend
r_1 c_1 a	9.9	7.8	
r_1 c_2 a	10.2	10.2	r_1 0.77 cm, radius
r_1 c_3 a	8.7	8.8	r_2 0.65 cm, radius
r_2 c_1 a	11.5	11.8	r_3 0.52 cm, radius
r_2 c_2 a	10.6	8.5	c_1 40 weight %
r_2 c_3 a	8.1	7.9	c_2 50 weight %
r_3 c_1 a	9.4	9.1	c_3 60 weight %
r_3 c_2 a	9.1	9.6	a absorption
r_3 c_3 a	8.2	8.4	d desorption
r_1 c_1 d	10.2	10.5	
r_1 c_2 d	11.8	11.6	
r_1 c_3 d	11.2	10.4	$10^6 \bar{D} = (10.0 \pm 0.20)$ cm^2 sec^{-1}
r_2 c_1 d	11.2	11.0	
r_2 c_2 d	11.1	10.4	
r_2 c_3 d	11.0	10.0	
r_3 c_1 d	11.9	8.3	
r_3 c_2 d	10.4	10.8	
r_3 c_3 d	9.4	9.5	

Conclusions of Statistical Analysis

(1) Method, m, is significant at 0.1% level.

(2) Interaction, cr, is significant at 5% level.

(3) Desorption occurs more quickly than absorption.

(4) D goes through a maximum at c_2.

(5) D goes through a maximum at r_2.

Conclusions (1), (4) and (5) differ from those for the "short time" results.

6.1.2. Results for Absorption and Desorption using V5 Cylinders

Table 6.10. "Short Time" Values of D for KCl - water

No. of Run	10^6 D (cm^2 sec^{-1})	Legend
r_1 c_1 a	8.83	
r_1 c_2 a	8.96	r_1 0.77 cm, radius
r_2 c_1 a	8.34	r_2 0.65 cm, radius
r_2 c_2 a	8.49	r_3 0.52 cm, radius
r_3 c_1 a	7.78	c_1 1N
r_3 c_2 a	8.12	c_2 3N
r_1 c_1 d	7.52	a absorption
r_1 c_2 d	7.19	d desorption
r_2 c_1 d	7.62	
r_2 c_2 d	7.55	10^6 D = (7.99 $\pm$ 0.14) cm^2 sec^{-1}.
r_3 c_1 d	7.58	
r_3 c_2 d	7.95	

Experiments were carried out at two initial solute concentrations, three cylinder radii, absorption and desorption, without repeats, i.e. a total of twelve experiments.

Conclusions of Statistical Analysis:

(1) Method, m, is significant at 5% level.

(2) No appreciable difference with increase in c.

(3) No appreciable difference with increase in r.

(4) Absorption occurs more quickly than desorption.

Table 6.11. "Short Time" Values of D for Sucrose-Water

No. of Run	10^6 D (cm^2 sec^{-1})	Legend
r_1 c_1 a	2.01	
r_1 c_2 a	2.10	r_1 0.77 cm, radius
r_2 c_1 a	2.09	r_2 0.65 cm, radius
r_2 c_2 a	2.03	r_3 0.52 cm, radius
r_3 c_1 a	2.03	c_1 15 weight %
r_3 c_2 a	2.02	c_2 30 weight %
r_1 c_1 d	2.32	a absorption
r_1 c_2 d	1.88	d desorption
r_2 c_1 d	2.05	
r_2 c_2 d	1.96	
r_3 c_1 d	2.13	$10^6 \bar{D} = (2.04 \pm 0.04)$ cm^2 sec^{-1}
r_3 c_2 d	1.89	

Experiments were carried out at two initial solute concentrations, three cylinder radii, absorption and desorption, without repeats, i.e. a total of 12 experiments.

Conclusions of Statistical Analysis

(1) No factor is significant at 5% level.

(2) Initial solute concentrations, c, is almost significant at 5% level.

(3) No appreciable difference between absorption and desorption.

(4) D decreases as c increases.

(5) D increases as cylinder radius, r, increases.

6.1.3. Results for Absorption and Desorption using CC2 Cylinders

Table 6.12. "Short Time" Values of D for KCl-Water

No. of Run	10^6 D (cm^2 sec^{-1})	Legend
r_2 c_1 a	6.06	
r_2 c_2 a	5.16	r_2 0.65 cm, radius
r_3 c_1 a	5.79	r_3 0.52 cm, radius
r_3 c_2 a	5.78	c_1 1N
r_2 c_1 d	5.52	c_2 3N
r_2 c_2 d	5.58	a absorption
r_3 c_1 d	5.35	d desorption
r_3 c_2 d	5.32	$10^6 \bar{D} = (5.70 \pm 0.14)$ cm^2 sec^{-1}

Experiments were carried out at two initial solute concentrations, two cylinder radii, absorption and desorption, without repeats, i.e. a total of eight experiments.

Conclusions of Statistical Analysis

(1) All factors are insignificant at 5% level.
(2) Method, m, is almost significant at 5% level.
(3) Absorption occurs more quickly than desorption.
(4) No difference in D as c increases.
(5) D increases as r increases.

Table 6.13. "Short Time" Values of D for Sucrose-Water

No. of Run	10^6 D (cm^2 sec^{-1})	Legend
r_2 c_1 a	1.64	
r_2 c_2 a	1.60	r_2 0.65 cm, radius
r_3 c_1 a	1.62	r_3 0.52 cm, radius
r_3 c_2 a	1.58	c_1 15 weight %
r_2 c_1 d	1.57	c_2 30 weight %
r_2 c_2 d	1.39	a absorption
r_3 c_1 d	1.44	d desorption
r_3 c_2 d	1.33	10^6 $\bar{D}$ = (1.52 ± 0.04) cm^2 sec^{-1}

Experiments were carried out at two initial solute concentrations, two radii, absorption and desorption, without repeats, i.e. a total of eight experiments.

Conclusions of Statistical Analysis

(1) No factor is significant at 5% level.
(2) Method, m, is almost significant at 5% level.
(3) Absorption occurs more quickly than desorption.
(4) D decreases as c increases.
(5) No appreciable variation in D as r increases.

6.1.4. Results for Desorption of KCl using Teflon Cylinders

The experiments with Teflon cylinders were the first experiments to be carried out using the recording balance. The experiments were carried out at two initial solute concentrations, two radii, and two water flowrates, without repeats, i.e. a total of eight experiments.

Table 6.14. "Short Time" Values of D for KCl-Water

No. of Run	10^6 D (cm^2 sec^{-1})	Legend
r_1 Re_1 c_1	5.4	
r_1 Re_1 c_2	6.2	r_1 0.52 cm, radius
r_2 Re_1 c_1	4.1	r_2 0.65 cm, radius
r_2 Re_1 c_2	8.1	Re_1 (annulus) 100
r_1 Re_2 c_1	4.4	Re_2 (annulus) 700
r_1 Re_2 c_2	5.2	c_1 1N
r_2 Re_2 c_1	5.0	c_2 3N
r_2 Re_2 c_2	8.9	$10^6 \bar{D} = (5.9 \pm 0.4)$ cm^2 sec^{-1}

Conclusions of Statistical Analysis

(1) Interaction c r is significant at 5% level.

(2) D increases as c increases.

(3) D is independent of the value of Re (annulus)

(4) D increases as r increases.

(5) Experimental error (obtained from duplicates of six of the runs) is high ($\pm$ 7% of mean).

6.1.5. Values of D at Different Reynolds Numbers

Desorption experiments were carried out using sucrose-water and the three ceramic materials to determine the effect on the diffusion coefficient of the flow regime outside the porous cylinder. Experiments were carried out at four levels of the Reynolds Number in the annulus between the cylinder and the glass wall of the diffusion tube. The concentration of the impregnating solution was 30 weight per cent sucrose.

The results are given in Table 6.15.

Table 6.15. Values of D for Sucrose-Water

Re (annulus) Reynolds Number	Material	10^6 D (cm^2 sec^{-1})		
		H.125	V5	CC2
2,000		2.53	1.91	1.60
3,500		2.63	2.01	1.41
4,700		2.47	1.86	1.32
7,100		2.84	1.74	1.56

Inspection of Table 6.15 indicates that Reynolds Number has no effect on the value of D. Although, due to lack of time, no duplicates were carried out, the experimental error, caused mainly by pulsing of the liquid affecting the plot on the recording balance chart, was high and would probably account for the variation in D for one porous material.

6.2. Calculated Values of the Ratio of the Diffusivity in Free Solution to the Diffusivity in the Porous Media

The ratio $\frac{D\ (\text{free solution})}{D\ (\text{porous medium})}$ has been given the symbol K^2 and may be termed the tortuosity factor. It has been suggested that K is the ratio of the actual distance travelled by the diffusing particle to the minimum geometrical distance.

Since analysis of the experimental results has shown that in most of the systems examined, there exist either interactions between concentration, radius, and method of sorption, or a dependence on radius or method, it would be meaningless to quote values of K^2 derived from mean values of D. Instead, values of K^2 are quoted at r_2, nominal radius 0.65 cm, and the initial solute concentration and method of sorption are also stated.

Table 6.16. Calculated Values of K^2 using Cylinders, Radius 0.65 cm.

Solute	Potassium Chloride			Sucrose		Carbon Tetrachloride		
Initial Solute Concentration	Normality			Weight %		Weight %		
	1	2	3	15	30	40	50	60
10^6 Diffusivity in Free solution (cm^2 sec^{-1})	18.8	20.1	21.1	4.2	3.2	16.6	15.0	13.4
Porous Material								
CC_2 absorption	3.10		3.43	2.56	2.00			
CC_2 desorption	3.41		3.78	2.68	2.30			
H125 absorption	1.71	1.81	1.95	1.48	1.09	1.60	1.61	1.56
H125 desorption	1.69	1.83	2.11	1.53	1.22	1.63	1.53	1.54
V5 absorption	2.25		2.49	2.01	1.58			
V5 desorption	2.47		2.79	2.05	1.63			
Teflon desorption	4.1		2.5					

6.3. Calculated Values of the Ratio of the Experimental Diffusivity, D, Divided by the Fractional Porosity of the Individual Cylinder

Introduction

From Fig. 24, it can be seen that there is a strong dependence of diffusivity on the porosity of the porous media. For this reason it was decided to define

$$D^1 = \frac{D \text{ (experimental)} \times 100}{\text{Individual cylinder porosity}} \quad (cm^2\ sec^{-1})$$

The values of D^1 were statistically analysed and graphs of D^1 vs the properties of the solute-solvent system and the porous media were drawn (see Figs. 17 - 30).

In the Tables below, only the "short time" values of D were used to give calculated values of D^1.

The statistical analysis of the D^1 values for the system CCl_4-methanol is given in appendix 5.

6.3.1. Values of D^1 using Hi25 Cylinders

Table 6.17. Values of D^1 for KCl-Water

No. of Run	10^6 D^1 (cm^2 sec^{-1})	10^6 D^1 repeat (cm^2 sec^{-1})	Legend
r_1 c_1 a	21.7	20.8	
r_1 c_2 a	21.9	21.6	r_1 0.77 cm, radius
r_1 c_3 a	20.9	23.6	r_2 0.65 cm, radius
r_2 c_1 a	21.7	21.9	r_3 0.52 cm, radius
r_2 c_2 a	21.4	21.9	c_1 1N
r_2 c_3 a	21.0	20.6	c_2 2N
r_3 c_1 a	25.3	24.0	c_3 3N
r_3 c_2 a	24.7	22.8	a absorption
r_3 c_3 a	24.9	23.1	d desorption
r_1 c_1 d	21.5	21.0	
r_1 c_2 d	20.8	22.4	
r_1 c_3 d	20.6	19.8	
r_2 c_1 d	22.1	21.2	
r_2 c_2 d	22.1	20.8	
r_2 c_3 d	20.9	18.9	
r_3 c_1 d	25.1	26.8	
r_3 c_2 d	25.7	24.1	
r_3 c_3 d	23.0	24.6	

Conclusions of Statistical Analysis

(1) Radius r, is significant at 0.1% level.

(2) Absorption occurs more quickly than desorption.

(3) D^1 decreases as initial solute concentration c increases.

(4) D^1 goes through a minimum at radius r_2.

Table 6.18. Values of D^1 for Sucrose-Water

No. of Run	$10^6 D^1$ (cm^2 sec^{-1})	Legend
r_1 c_1 a	5.44	
r_1 c_2 a	5.19	r_1 0.77 cm, radius
r_2 c_1 a	5.46	r_2 0.65 cm, radius
r_2 c_2 a	5.63	r_3 0.52 cm, radius
r_3 c_1 a	5.90	c_1 15 weight %
r_3 c_2 a	5.24	c_2 30 weight %
r_1 c_1 a	5.19	a absorption
r_1 c_2 d	5.05	d desorption
r_2 c_1 d	5.27	
r_2 c_2 d	5.06	
r_3 c_1 d	5.90	
r_3 c_2 d	5.28	

Conclusions of Statistical Analysis

(1) Initial solute concentration, c, significant at 5% level.

(2) Absorption occurs more quickly than desorption.

(3) D^1 decreases as c increases.

(4) D^1 decreases as r increases.

Table 6.19. Values of D^1 for Carbon Tetrachloride-Methanol

No. of Run	$10^6 D^1$ (cm^2 sec^{-1})	$10^6 D^1$ repeat (cm^2 sec^{-1})	Legend
r_1 c_1 a	19.5	19.4	
r_1 c_2 a	19.9	20.0	
r_1 c_3 a	16.8	17.4	r_1 0.77 cm, radius
r_2 c_1 a	19.2	20.9	r_2 0.65 cm, radius
r_2 c_2 a	18.8	16.8	r_3 0.52 cm, radius
r_2 c_3 a	16.7	16.4	c_1 40 weight %
r_3 c_1 a	20.6	19.1	c_2 50 weight %
r_3 c_2 a	17.9	19.3	c_3 60 weight %
r_3 c_3 a	17.1	16.2	a absorption
r_1 c_1 d	19.9	20.0	d desorption
r_1 c_2 d	21.4	20.7	
r_1 c_3 d	19.9	19.8	
r_2 c_1 d	19.2	19.9	
r_2 c_2 d	18.8	18.8	
r_2 c_3 d	16.5	17.0	
r_3 c_1 d	20.4	19.8	
r_3 c_2 d	19.8	18.9	
r_3 c_3 d	18.9	18.1	

Conclusions of Statistical Analysis

(1) Interactions cm and cr, are significant at 5% level.

(2) Desorption occurs more quickly than absorption.

(3) D^1 decreases as c increases.

(4) D^1 goes through a minimum at radius r_2.

6.3.2. Values of D^1 using V5 Cylinders

Tables 6.20 Values of D^1 for KCl-Water

No. of Run	$10^6 D^1$ (cm^2 sec^{-1})	Legend
r_1 c_1 a	21.0	
r_1 c_2 a	21.8	r_1 0.77 cm, radius
r_2 c_1 a	19.7	r_2 0.65 cm, radius
r_2 c_2 a	20.0	r_3 0.52 cm, radius
r_3 c_1 a	18.1	c_1 1N
r_3 c_2 a	18.8	c_2 3N
r_1 c_1 d	17.9	a absorption
r_1 c_2 d	17.1	d desorption
r_2 c_1 d	18.0	
r_2 c_2 d	17.8	
r_3 c_1 d	17.6	
r_3 c_2 d	17.5	

Conclusions of Statistical Analysis

(1) Method, m, is significant at 1% level.

(2) Absorption occurs more quickly than desorption.

(3) No appreciable difference in D^1 as c increases.

(4) D^1 increases as r increases.

Table 6.21. Values of D^1 for Sucrose-Water

No. of Run	10^6 D^1 (cm^2 sec^{-1})	Legend
r_1 c_1 a	4.77	
r_1 c_2 a	4.99	r_1 0.77 cm, radius
r_2 c_1 a	4.93	r_2 0.65 cm, radius
r_2 c_2 a	4.79	r_3 0.52 cm, radius
r_3 c_1 a	4.71	c_1 15 weight %
r_3 c_2 a	4.69	c_2 30 weight %
r_1 c_1 a	5.51	a absorption
r_1 c_2 d	4.47	d desorption
r_2 c_1 d	4.83	
r_2 c_2 d	4.62	
r_3 c_1 d	4.94	
r_3 c_2 d	4.39	

Conclusions of Statistical Analysis

(1) Interaction cm significant at 5% level.

(2) No appreciable difference between absorption and desorption.

(3) D^1 decreases as c increases.

(4) D^1 increases as r increases.

6.3.3. Values of D^1 using CC2 Cylinders

Tables 6.22. Values of D^1 for KCl-Water

No. of Run	10^6 D^1 (cm^2 sec^{-1})	Legend
r_2 c_1 a	15.7	
r_2 c_2 a	16.0	r_2 0.65 cm, radius
r_3 c_1 a	15.4	r_3 0.52 cm, radius
r_3 c_2 a	15.4	c_1 1N
r_2 c_1 d	14.3	c_2 3N
r_2 c_2 d	14.5	a absorption
r_3 c_1 d	14.3	d desorption

Conclusions of Statistical Analysis

(1) No factors significant at 5% level.
(2) Absorption occurs more quickly than desorption.
(3) No appreciable difference in D^1 as c increases.
(4) No appreciable difference in D^1 as r increases.

Table 6.23. Values of D^1 for Sucrose-Water

No. of Run	10^6 D^1 (cm^2 sec^{-1})	Legend
r_2 c_1 a	4.26	
r_2 c_2 a	4.16	r_2 0.65 cm, radius
r_3 c_1 a	4.32	r_3 0.52 cm, radius
r_3 c_2 a	4.21	c_1 15 weight %
r_2 c_1 d	4.08	c_2 30 weight %
r_2 c_2 d	3.61	a absorption
r_3 c_1 d	3.84	d desorption
r_3 c_2 d	3.55	

Conclusions of Statistical Analysis

(1) Method, m, is significant at 1% level.
(2) Absorption occurs more quickly than desorption.
(3) D^1 decreases as c increases.
(4) No appreciable difference in D^1 as r increases.

Inspection of the Table of D^1 indicates that, over the complete range of porous media, the diffusivity, D, is not dependent on the porosity alone. The dependence is more complex and the values of D and D^1 indicate that D is dependent on a combination of porosity and pore size distribution. Total porosity appeared to influence the relative values of D for V5 and H125 cylinders while

both the porosity and pore size distribution appeared to influence the relative values of D for H125 and CC2 cylinders.

As a test, values of D and D^1 at levels r_2 c_2 a, r_2 c_2 d, r_2 c_1 a, r_2 c_1 d, r_3 c_2 a, and r_3 c_2 d were taken for the solute-solvent systems of KCl-water and sucrose-water. The ratios of the D values and of the D^1 values were compared with the ratios of total porosity and pore size parameters.

The results at levels r_2 c_2 a and r_2 c_2 d are shown in Tables 6.24 and 6.25 below.

Table 6.24. Comparison of Results using V5 and H125 Cylinders

Material	Mean Porosity (%)	Mean Pore Diameter (μ)	10^6 D (cm^2 sec^{-1})				10^6 D^1 (cm^2 sec^{-1})			
			KCl		Sucrose		KCl		Sucrose	
			a	d	a	d	a	d	a	d
H125	51.3	1.0	11.1	11.0	2.93	2.63	21.7	21.5	5.63	5.16
V5	42.5	4.0	8.49	7.55	2.03	1.96	20.0	17.8	4.79	4.62
Ratio	1.21	0.25	1.31	1.46	1.44	1.34	1.09	1.21	1.18	1.10

Legend a - absorption; d - desorption.

From Table 6.24 it is seen that the ratio $\frac{D^1 \text{ (H125)}}{D^1 \text{ (V5)}}$ is almost equal to the ratio of the porosities.

The values at levels r_2 c_1 a, r_2 c_1 d, r_3 c_2 a and r_3 c_2 d are similar to those in Table 6.24 and therefore, for coarse pores it is suggested that D is a function of the square of the porosity of the porous medium.

Table 6.25. Comparison of Results using H125 and CC2 Cylinders

Material	Mean Porosity (%)	Mean Pore Diameter (μ)	B (%)	P (%)	10^6 D ($cm^2 sec^{-1}$)				10^6 D^1 (cm^2 sec^{-1})			
					KCl		Sucrose		KCl		Sucrose	
					a	d	a	d	a	d	a	d
H125	51.3	1.0	25	49.5	11.1	11.0	2.93	2.63	21.7	21.5	4.63	5.06
CC2	39.0	0.45	38.5	97.8	6.16	5.58	1.60	1.39	16.0	14.5	4.16	3.61
Ratio	1.32	2.22			1.79	1.97	1.83	1.89	1.36	1.48	1.35	1.40
Inverse Ratio			1.54	1.98								

Legend a - absorption, d - desorption

B - % Bulk Volume less than 1μ diameter

P - % Pore Volume less than 1μ diameter

The figures in Table 6.25 and the similar figures at the other levels suggest that the ratio of $\frac{D\ (H125)}{D\ (CC2)}$ is almost inversely proportional to the ratio of P.

Therefore, for fine pores, it is suggested that D is a function of the percentage of the pore volume occupied by pores less than 1μ diameter.

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7. DISCUSSION OF THE EXPERIMENTAL RESULTS

7.0 INTRODUCTION

The results will be discussed under ten headings, which, for convenience, are presented in three groups. The groups are as follows:-

GROUP I. GENERAL DISCUSSION

(1) The aims of factorial experiments and explanation of the statistical terms used in the text.

(2) Comparison of the results obtained by the three experimental methods.

(3) Consistency and accuracy of the experimental results.

GROUP II. EFFECT OF THE EXPERIMENTAL VARIABLES

(4) Method of sorption.

(5) Initial solute concentration.

(6) Radius of porous cylinder.

(7) Flow conditions outside the porous cylinder.

GROUP III. EFFECT OF RELATED PARAMETERS

(8) Diameter of the diffusing particle.

(9) Properties of the porous media.

(10) Interaction of the diffusing particle and the porous medium.

7.1. The Aims of the Factorial Experiments and an Explanation of the Statistical Terms used in the Text

Factorial experiments are experiments which are carried out at different planned levels of the independent variables.

A group of experiments carried out by the author will be used to illustrate this. The effect of the variables, cylinder radius (r), method of sorption (m) and initial solute concentration (c), on the mutual diffusivity, (D) was required. The simplest factorial experiment would require runs at the following levels:-

$r_1\ c_1\ a$	$r_1\ c_1\ d$
$r_1\ c_2\ a$	$r_1\ c_2\ d$
$r_2\ c_1\ a$	$r_2\ c_1\ d$
$r_2\ c_2\ a$	$r_2\ c_2\ d$

where r_1 = radius 1
r_2 = radius 2
c_1 = concentration 1
c_2 = concentration 2
a = absorption
d = desorption

i.e. two levels of each variable making a total of eight runs.

The aims of factorial experiments are:-

(1) To obtain the maximum amount of information from the minimum number of experimental runs.

(2) To detect the interaction of variables, e.g. the effect on D of a change from c_1 to c_2 may not be the same for absorption and desorption. Then there exists an interaction cm.

The classical experiment gives less information from a given number of runs and in many cases would not be designed to show up interactions which exist.

In a factorial series of experiments the experimental error or the related experimental variance gives a statistical estimate of the error between duplicate runs. The experimental variance was determined by one of two methods, which are described below.

(a) When repeats were carried out for every run in the series, the experimental variance was determined from the squares of the differences between run and repeat. The details are given in Appendix 4.

(b) When repeats were not carried out for every run in the series, repeats of certain runs were carried out and the experimental variance determined from the squares of the difference between run and repeat. The details are given in Appendices 4 and 5.

Explanation of Terms used in Statistical Analysis

A complete statistical analysis of one factorial series is given in Appendix 4, but certain important points are noted here.

(1) The effects of the variables and the interactions are compared with the experimental variance. The ratio of the mean square of the variable or interaction to the experimental variance is called F.

(2) A variable or interaction is significant at a certain level if the value of F is greater than that quoted in the statistical tables for the stated number of degrees of freedom.

If, for example, method m, is significant at the 5% level, this means that there is 95% probability that the change in D is due to the effect of m and 5% probability that it is due to random chance. Similarly, if m is significant at the 1% level, there is 99% probability that the change in D is due to the effect of m and 1% probability that it is due to random chance.

7.2. Comparison of the Results Obtained from Three Different Experimental Methods

The system potassium chloride (K.Cl) - water with H125 cylinders was studied by three experimental methods. The mean values of D, given the symbol $\bar{D}$, and the estimate of the experimental error are given in Table 7.1.

Table 7.1. Comparative Values of $\bar{D}$ for K Cl-Water-H125

Experimental Method	$10^6 \bar{D}$ ($cm^2\ sec^{-1}$) Short Time	10^6 experimental error ($cm^2\ sec^{-1}$) Short Time
Recording balance	10.80	0.10
Capacitance Cell	12.3	0.4
Conductivity Cell	10.20	0.14

As explained in 6.1.1.3, the considerable experimental difficulties using the capacitance cell demonstrated that the method was not very accurate and too much attention should not be paid to the absolute value of D thus obtained. However it should be noted that the value of D from the capacitance cell is of the same order as that from the recording balance, and, to that extent, acts as a check.

The values of D obtained using the conductivity cell were much more consistent than those obtained using the capacitance cell and the same variation of D with radius was observed.

Although the difference between the mean values of D obtained by the two methods is outwith the experimental errors quoted, it is small.

The values of D from the two methods agree to within 4% of the mean value.

7.3. Accuracy of the Experimental Results

Since the experimental error of the three experimental methods of determining D for KCl-water-H125 was approximately the same and since much more experimental work has been done with the recording balance, only the results obtained using the recording balance will be considered here.

Regarding the consistency of the results, it should be noted that in a factorial series, if a run was thought or known to be experimentally inaccurate, the run was repeated. But provided there was no experimental reason for doubting a result, it stood.

The experimental variance, σ^2, is a measure of the experimental error and is defined as:-

$$\sigma^2 = \frac{d^2 - 1/n\ (\Sigma d)^2}{n - 1}$$

where d = difference in values of D for run and its repeat

n = number of runs.

The experimental error, E, is defined as $\frac{\sigma}{\sqrt{n}}$

The values of the mean diffusivity $\bar{D}$, and the experimental error, E, of all the systems studied, are given in Table 7.2.

Table 7.2. Values of $\bar{D}$ and E

Porous Material	Solute-Solvent System	$10^6 \bar{D}$ (cm^2 sec^{-1})		10^6 D (cm^2 sec^{-1})	
		Short Time	Long Time	Short Time	Long Time
H125	KCl-water	11.30	11.6	0.14	0.3
H125	Sucrose-water	2.79		0.04	
H125	CCl_4-methanol	9.77	10.0	0.08	0.2
V5	KCl-water	7.99		0.14	
V5	Sucrose-water	2.04		0.04	
CC2	KCl-water	5.70		0.14	
CC2	Sucrose-water	1.52		0.04	
Teflon	KCl-water	5.9		0.4	

The experimental errors were determined as follows:

(1) KCl-water. Eighteen runs with repeats were carried out using H125 cylinders. The value of E obtained from statistical analysis was used in the analysis of results using V5 and CC2 cylinders.

(2) Sucrose-water. Eight absorption runs with repeats were carried out using H125, V5 and CC2 cylinders. The concentration in the circulating solution was 15 weight % sucrose. The value of E so obtained was used for all runs involving the system sucrose-water.

(3) Carbon tetrachloride (CCl_4)-methanol. Eighteen runs with repeats were carried out using H125 cylinder and the value of E was obtained from the statistical analysis.

The method of determining E assumes that the error is the same for each porous material but varies with the solute-solvent system. The experimentally determined quantities were ΔW, the apparent change in weight

of the cylinder between times t_1 and t_2 and Mo or M_∞, the mass of solute desorbed or absorbed after infinite time. ΔW might be affected by the surface tension of the circulating solution and an error in Mo or M_∞ might be caused by evaporation of the impregnating solution e.g. there will be more evaporation when the impregnating solution is carbon tetrachloride-methanol than when it is KCl-water. Thus the experimental error, will be affected by the solute-solvent system.

Because of the method of determining the experimental error, the % experimental error of the mean has limited significance. However, Table 7.3 gives the % error about the mean for H125 cylinders.

Table 7.3. Percentage Experimental Error using H125 Cylinders

Solute-Solvent System	$10^6 \bar{D}$ (cm^2 sec^{-1}) "short time"	% Error about mean
KCl-water	11.30	1.2
Sucrose-water	2.79	1.4
CCl_4-methanol	9.77	0.8

From Table 7.3 it can be seen that the experimental error is approximately 1%.

The slightly higher value for sucrose-water can be explained as an inaccuracy in ΔW, since the weight changes with sucrose were much smaller than with KCl-water or CCl_4-methanol and there is a greater probability of the surface tension force causing an error.

The percentage error is considerably smaller for CCl_4-methanol than for the other systems. The only difference in experimental technique was that, since the impregnating solution was so volatile, the cylinder was not wiped with a cloth but was immediately placed in a tared aluminium container.

Thus it is very probable that the wiping of the porous cylinders constitutes a random error.

Taking the maximum percentage error as 1.4%, it can be concluded that the experiments carried out by the author were more accurate than those of Stewart (44) whose percentage error was 3.5%.

MacDonald (10) did not give a value for the percentage error but this author's estimate of his error is 6% approximately.

7.4. Effect of Method of Sorption

The relevant conclusions of the statistical analyses are summarised in Table 7.4. Unless otherwise stated the values of D are calculated using the "short time" solution.

Porous Material	Solute-Solvent System	Conclusions of statistical analysis
H125 (short time)	KCl-water	No difference between absorption and desorption.
H125 (long time)	KCl-water	No difference between absorption and desorption.
H125	Sucrose-water	Absorption is quicker than desorption.
H125 (short time)	CCl_4-methanol	Desorption is quicker than absorption.
H125 (long time)	CCl_4-methanol	Desorption is quicker than absorption. Method significant at 0.1% level.
V5	KCl-water	Method significant at 5% level. Absorption is quicker than desorption.
V5	Sucrose-water	No difference between absorption and desorption.
CC2	KCl-water	Method is almost significant at 5% level. Absorption is quicker than desorption.
CC2	Sucrose-water	Method is almost significant at 5% level. Absorption is quicker than desorption

Before discussing the meaning of Table 7.4. it must be emphasised that whenever an interaction, which involves a variable, is statistically significant, the effect of that variable alone is considerably modified and it is unwise to attach too much significance to the effect of the variable.

Neglecting the series (a) H125 (short time) - KCl-water and (b) H125 (short time) - CCl-methanol since the interaction cm is significant or almost so at the 5% level, the following observations can be made:-

(1) There is a significant difference between the aqueous solutions and the organic solution. For aqueous solutions the rate of absorption is either equal to or greater than the rate of desorption whereas for the organic solution the rate of desorption is greater than the rate of absorption and most decidedly so (significant at 0.1% level).

(2) Considering the results for the aqueous solutions in greater detail, the trend is for absorption to be greater than desorption irrespective of the porous material. Even for the series H125-KCl-water and V5-sucrose-water, although there is no appreciable difference between absorption and desorption, the figures show that absorption is slightly greater than desorption.

So, for the two aqueous solutions studied, absorption is greater than desorption and, in general, the method of sorption becomes more significant as the porosity of the porous medium decreases.

Crank and Henry (5) predicted that the relative rates of absorption and desorption would depend on the variation of the diffusivity in free solution with concentration.

The dependence of the diffusivity in free solution with concentration, for the three systems investigated, is summarised below:-

KCl-water: D decreases from 2.0×10^{-5} cm^2 sec^{-1} at infinite dilution to a minimum of 1.82×10^{-5} cm^2 sec^{-1} at approximately 0.1N and then increases linearly to 2.10×10^{-5} cm^2 sec^{-1} at 3N.

Sucrose-water: D decreases approximately linearly from 5.2×10^{-6} cm^2 sec^{-1} at infinite dilution to 0.7×10^{-6} cm^2 sec^{-1} at 70 weight % sucrose.

Carbon tetrachloride-methanol: D decreases linearly from 1.82×10^{-5} cm^2 sec^{-1} at 30 weight % CCl_4 to 1.18×10^{-5} cm^2 sec^{-1} at 70 weight % CCl_4.

As applied to the three systems being studied, the predictions of Crank and Henry are:-

KCl-water: Provided the mean concentration is greater than 0.1N, absorption should be quicker than desorption.

Sucrose-water: Desorption should be quicker than absorption.

Carbon tetrachloride-methanol: Desorption should be quicker than absorption.

The experimental results for KCl-water and CCl_4-methanol agree with these predictions but the results for sucrose-water do not.

It is difficult to determine where the discrepancy arises in the theoretical predictions or in the sucrose-water experimental results - as only three solute-solvent systems were examined.

The results of MacDonald indicated that there was no appreciable difference between absorption and desorption for KCl-water, but that desorption was greater than absorption for sucrose-water. The difference between the results of MacDonald and the author for sucrose-water may be accounted for by MacDonald's large experimental error.

7.5. Effect of Initial Solute Concentration

The relevant conclusions of the statistical analyses are summarised in Table 7.5.

Unless otherwise stated the values of D are calculated using the "short time" solution.

To avoid unnecessary repetition, c, "concentration" will be used throughout instead of initial solute concentration.

TABLE 7.5

Porous Material	Solute-Solvent System	Conclusions of Statistical Analysis
H125 (short time)	KCl-water	D decreases as c increases.
H125 (long time)	KCl-water	c almost significant at 5% level. D goes through a maximum at c_2.
H125	Sucrose-water	c almost significant at 5% level. D decreases as c increases.
H125 (short time)	CCl_4-methanol	D decreases as c increases.
H125 (long time)	CCl_4-methanol	D goes through a maximum at c_2.
V5	KCl-water	Slight increase with c.
V5	Sucrose-water	c is almost significant at 5% level. D decreases as c increases.
CC2	KCl-water	Slight increase with c.
CC2	Sucrose-water	Slight decrease as c increases.

Neglecting series H125 (short time) - KCl-water, H125 (short time) - CCl_4-methanol, and H125 (long time) - CCl_4-methanol, since interactions cm or cr are significant at the 5% level, the following observations can be made:-

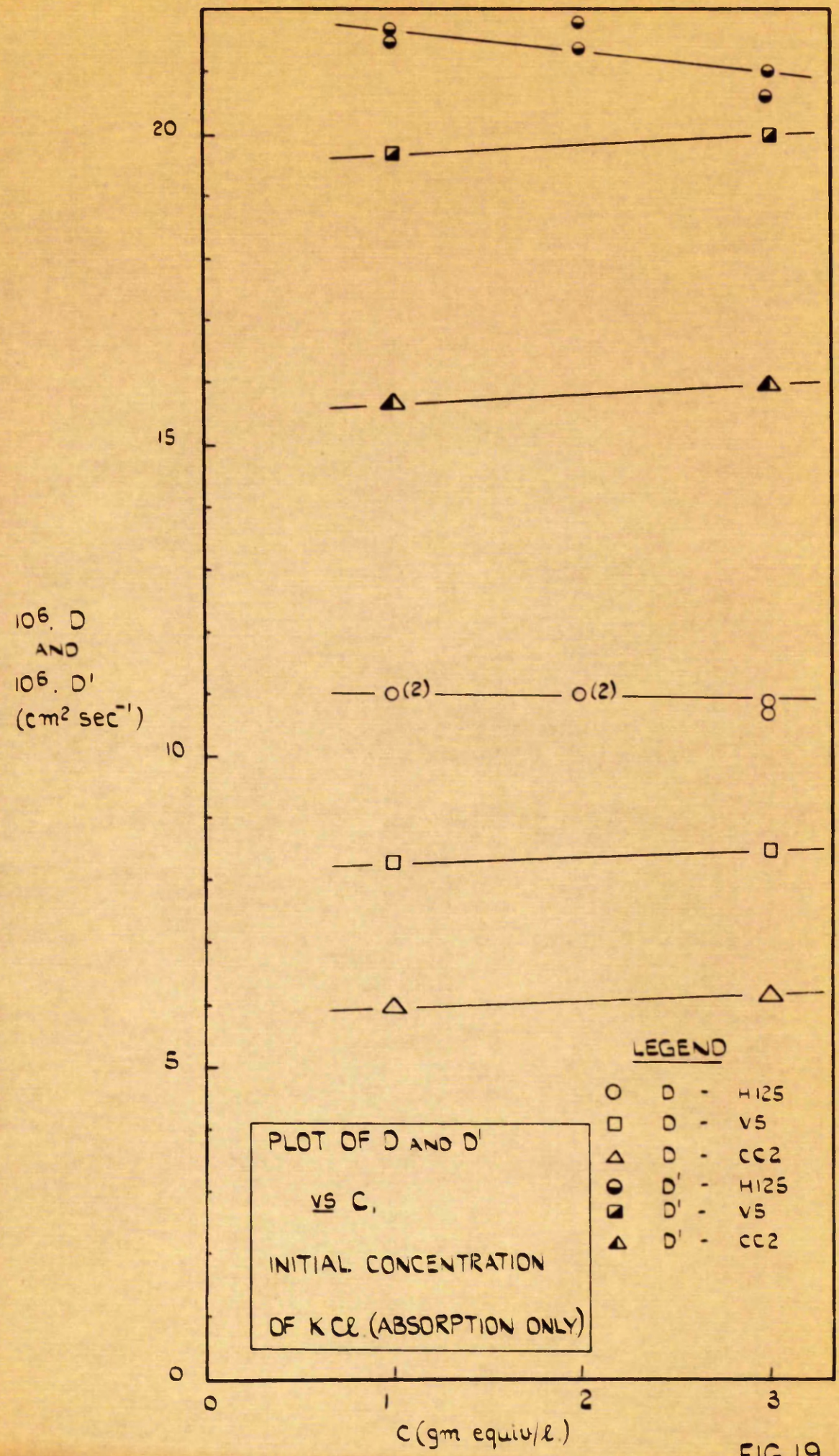
20
15
10
5
0
0
1
2
3
10^6. D AND 10^6. D' ($cm^2\ sec^{-1}$)
C (gm equiv/ℓ.)
O(2)
O(2)
8
LEGEND
D - H125
D - VS
D - CC2
D' - H125
D' - VS
D' - CC2
PLOT OF D AND D' VS C, INITIAL CONCENTRATION OF KCℓ (ABSORPTION ONLY)

FIG. 19

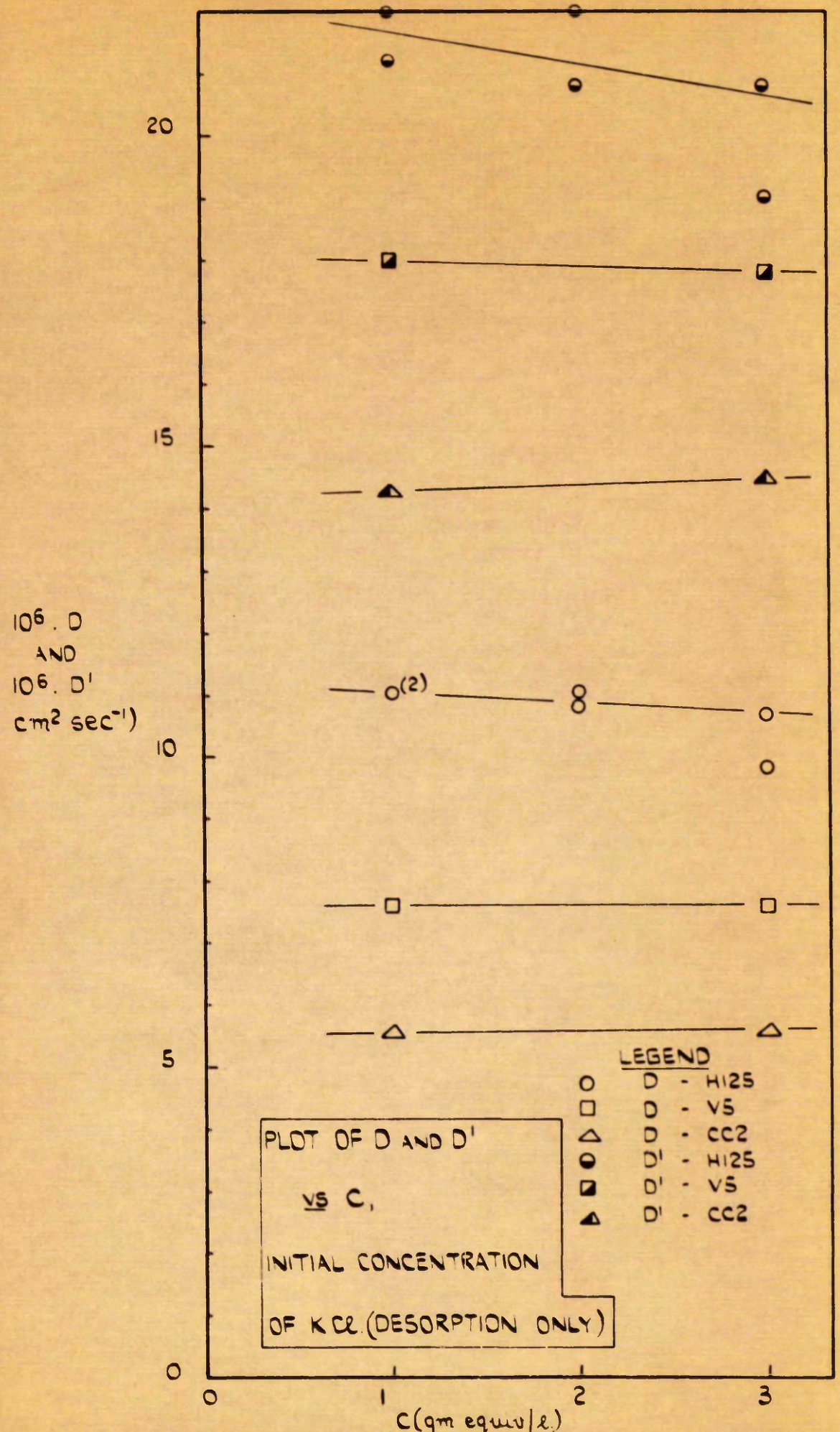
20
15
10
5
0
0
1
2
3
10^6. D AND 10^6. D' $cm^2\ sec^{-1}$)
C(gm equiv/ℓ)
LEGEND
D - H125
D - V5
D - CC2
D' - H125
D' - V5
D' - CC2
PLOT OF D AND D' VS C, INITIAL CONCENTRATION OF KCℓ (DESORPTION ONLY)

FIG. 20

PLOT OF D AND D' vs C,

INITIAL CONCENTRATION OF SUCROSE

(ABSORPTION ONLY)

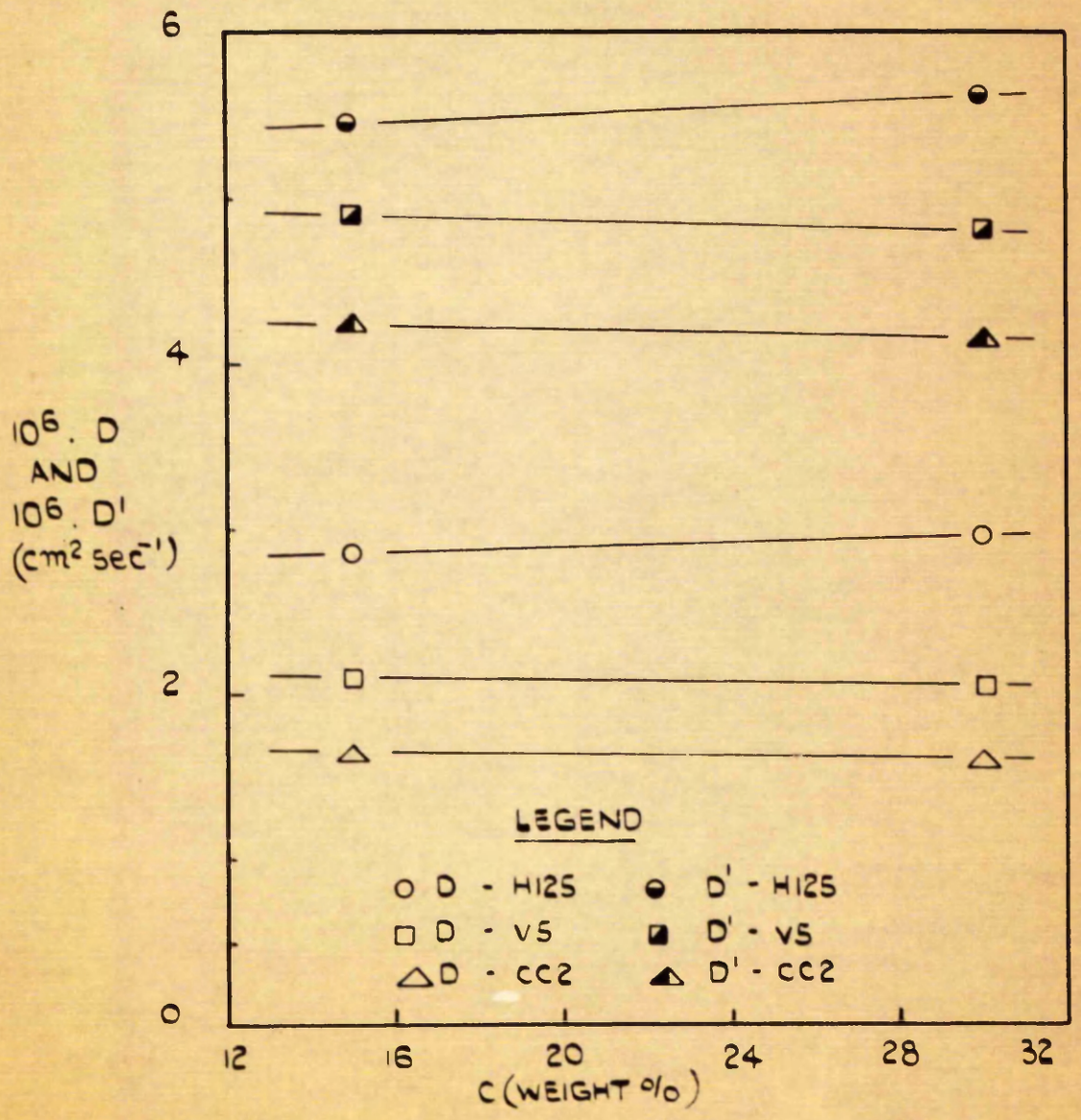

FIG. 21.

PLOT OF D AND D' vs C,

INITIAL CONCENTRATION OF SUCROSE

(DESORPTION ONLY)

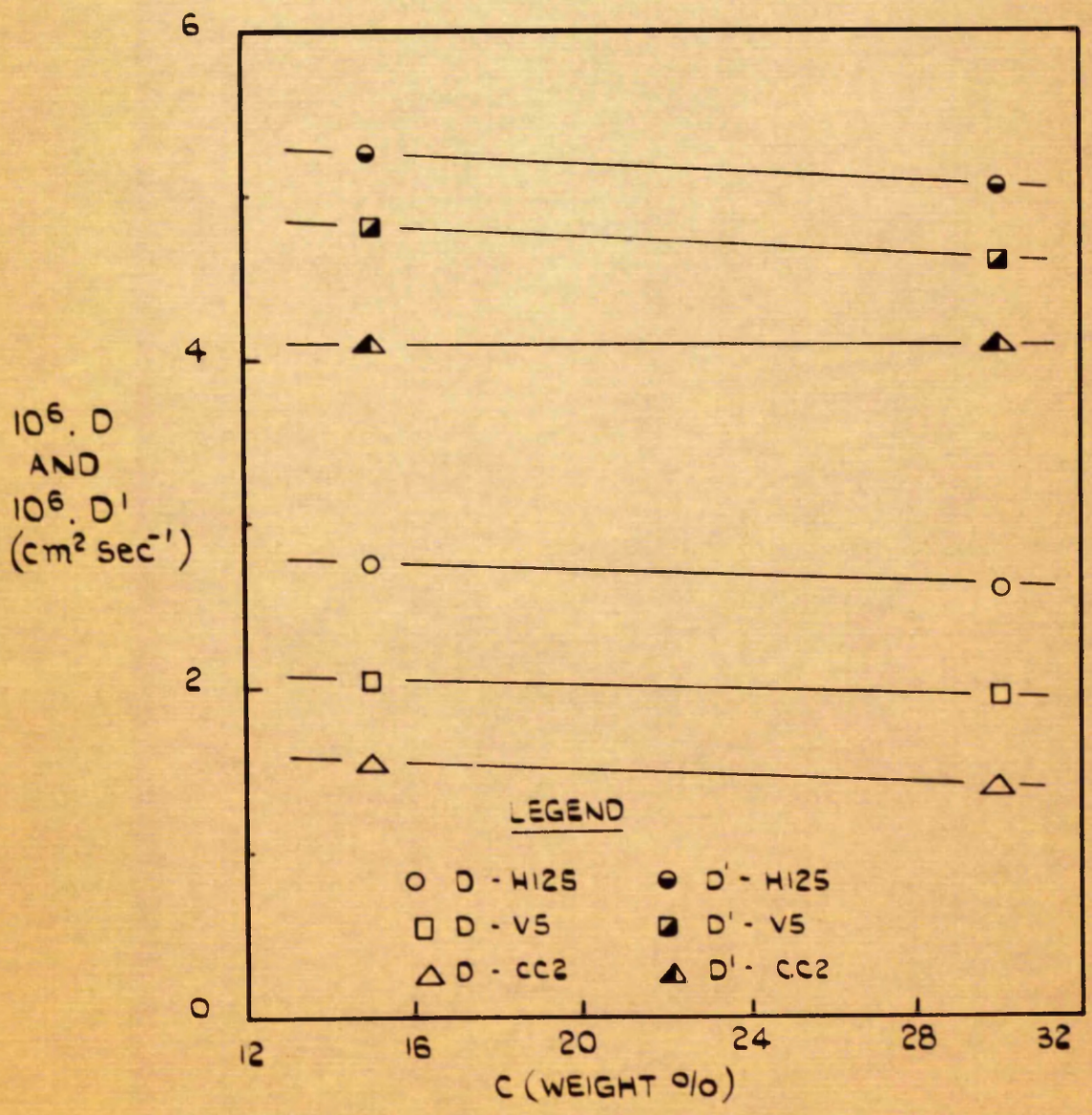

FIG. 22.

INITIAL CONCENTRATION OF
CARBON TETRACHLORIDE

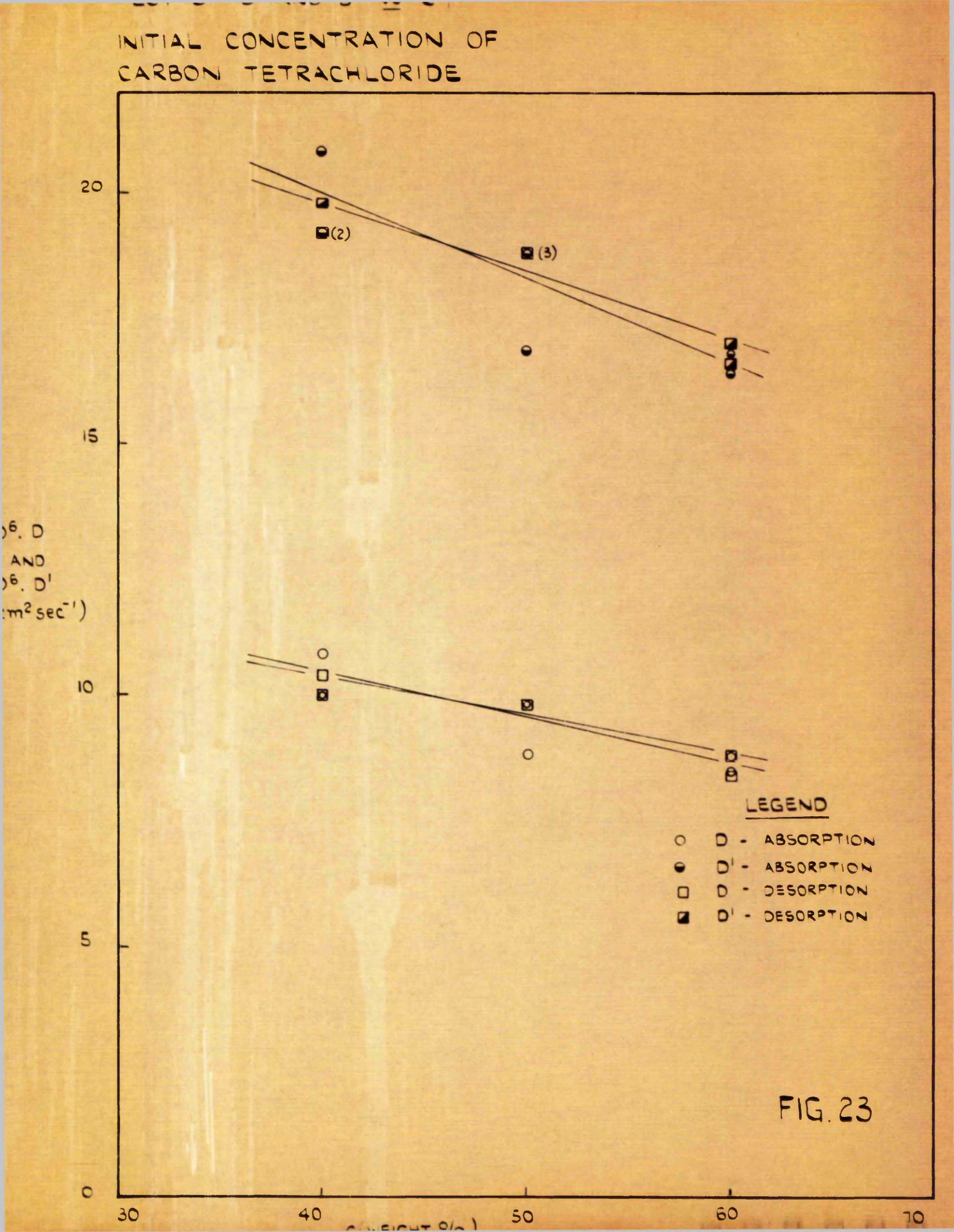

FIG. 23

(1) KCl-water: With the exception of the "long time" solutions for H125 cylinders where D goes through a maximum at concentration c_2, D shows a slight increase as c increases.

(2) Sucrose-water: For all three porous materials, D decreases as c increases.

Thus, in the cases where interactions involving c are not significant at the 5% level, the diffusivity in porous media varies with concentration in the same way as the diffusivity in free solution.

The above observations agree with those of Stewart (44) who, investigating the diffusion in porous media of aqueous solutions of hydrochloric acid (HCl), potassium chloride (KCl), and lithium chloride (Li Cl), concluded that the diffusivity in porous media of these systems varied with concentration in the same way as the diffusivity in free solution. MacDonald (10) also concluded that for KCl-water, the diffusivity in porous media behaved in the same way as the diffusivity in free solution.

7.6. Effect of Radius of Porous Cylinder

Cylinders of three nominal radii were used in the case of porous materials H125 and V5, but due to manufacturing difficulties, only two nominal radii were used in the case of CC2 cylinders. No mention of the dependence of D on the size of the porous material has been reported in the literature, so far as is known.

The relevant conclusions of the statistical analyses are given in Table 7.6.

TABLE 7.6

Porous Material	Solute-Solvent System	Conclusions of Statistical Analysis
H125 (short time)	KCl-water	r is significant at 0.1% level. D decreases as r increases.
H125 (long time)	KCl-water	r is significant at 0.1% level. D goes through a minimum at radius r_2.
H125	Sucrose-water	D decreases as r increases.
H125 (short time)	CCl_4-methanol	D goes through a minimum at radius r_2.
H125 (long time)	CCl_4-methanol	D goes through a maximum at radius r_2.
V5	KCl-water	Slight increase with r.
V5	Sucrose-water	D increases as r increases.
CC2	KCl-water	D increases as r increases.
CC2	Sucrose-water	Slight increase with r.

In the series CCl_4-methanol-H125, using both "short time" and "long time" solutions, interaction cr was significant at the 5% level. Inspection of the statistical table for the "short time" solution showed that the results at radius r_1 were inconsistent with the trend of the other results. This anomalous effect was thought to be connected with the diameter of the annulus between the cylinder and the diffusion tube.

Both the series KCl-water - H125 and CCl_4 - methanol - H125, were carried out using a diffusion tube of inner diameter 2.0 cm. Thus for the porous cylinders of nominal radius r_1 = 0.77 cm, the diameter of the annulus is only 0.46 cm and the space between the wall of the diffusion tube and the porous cylinder is 0.23 cm. (radius

of annulus). It is possible, therefore, that the concentration could build up in the annular space and so change the boundary conditions used in solving the diffusion equation. For this reason, the results of both the above mentioned series were statistically analysed, neglecting the results at radius r_1. The conclusions of these analyses were:-

(1) H125 (short time) - KCl-water

(a) Radius r is significant at 0.1% level.
(b) Concentration c is significant at 5% level.
(c) No difference between absorption and desorption.
(d) D decreases as c increases.
(e) D decreases as r increases.

(2) H125 (short time) - CCl_4-methanol

(a) Radius r, is significant at 5% level.
(b) Concentration c is significant at 0.1% level.
(c) Desorption occurs more quickly than absorption.
(d) D decreases as c increases.
(e) D decreases as r increases.

The effect of neglecting results at radius r_1 is that interaction cr is no longer significant.

In the discussion of the effect of cylinder radius the above conclusions (1) and (2) will be taken and compared with the conclusions from results obtained using three radii for the other systems as the diameter of the diffusion tube was increased for the other systems. The inner diameter of the new diffusion tube was 3.9 cm. giving, for a cylinder of nominal radius r_1, 0.77 cm, a diameter of annulus = 2.36 cm and an annular space of 1.18 cm.

Conclusions: (1) The dependence of D on radius r differs with the porous material.

(2) For H125 cylinders D decreases as radius increases, particularly for the systems KCl-water and CCl_4-methanol.

(3) For V5 and CC2 cylinders, D increases as radius increases. The effect is not so marked as the effect for H125 cylinders.

The solute-solvent system appears to have little effect on the dependence of D on radius but the properties of the porous media have a marked effect on this dependence. The radius effect seems to be linked with the total porosity of the porous media. Examination of the pore entrance distribution curves shows that material H125 has little spread of pore entrance diameters, material CC2 is next, and material V5 has considerable spread of pore entrance diameters.

Both the V5 and CC2 cylinders are less porous than the H125 cylinders i.e. they are denser than the H125 cylinders. If, due to the manufacturing process of slip-casting, these cylinders (V5 and CC2) are not uniform throughout their complete radius but are denser in the centre, then there will be a preponderance of relatively coarse pores near the surface and of relatively fine pores towards the centre. The larger the radius, the more pronounced the effect. Hence, with small radius, the fine pores would contribute and reduce the measured rate of mass transfer and, with increase in radius, the effect of mass transfer from the fine pores would be reduced and the measured rate of mass transfer increased. Considerable difficulty was experienced in the manufacture of these cylinders, particularly the CC2 cylinders and, in fact, it was impossible to manufacture a CC2 cylinder of nominal radius $r_1 = 0.77$ cm. With regard to the H125 cylinders, the manufacturer had many years experience in manufacturing industrial filters with this material and the pore entrance size distribution curves verified that there was very little

spread in pore entrance diameters and that the duplicates were very consistent. It therefore seems reasonable to assume that the H125 cylinders are uniform throughout their radius, and so the decrease in D with increasing radius cannot be explained in the same way as the increase in D was for V5 and CC2 cylinders.

The results obtained from the conductivity cell for the system H125-KCl-water showed the same definite trend as the corresponding results using the recording balance.

There was no appreciable difference in D between cylinders at radius r_1 = 0.77 cm, r_2 = 0.65 cm. and r_4 = 0.38 cm. but the value of D at r_3 = 0.52 cm. was approximately (10 - 20%) higher than D at the other radii. This increase was of the same order but a little higher than that when D was determined using the recording balance.

The cylinders of radius r_3 had been used for preliminary experiments at varying lissapol flowrates and in order to acquire the experimental technique; and these experiments with their subsequent extractions using water at 100°C, must have leached the pores and enlarged them.

Therefore all results at radius r_3 for H125-KCl-water experiments must be neglected. It is then obvious that D does not vary at all with radius. The radius effect is not significant for H125-CCl_4-methanol as interaction or is significant at the 5% level.

7.7. Effect of Flow Conditions outside the Porous Cylinders

Since there was little evidence pointing to a dependence of the rate of mass transfer in porous media on the external flow conditions, only a short time was devoted to investigating this effect.

The preliminary KCl-water experiments using Teflon cylinders (see Table 6.14) though inaccurate showed that water flowrate had no effect on the value of D. The KCl-water experiments carried out using the capacitance cell and H125 cylinders (see Table 6.5) could not detect

any variation of D with water flowrate. Finally experiments using the recording balance and water flowrates to give Re (annulus) from 2,000 to 7,100 were carried out using sucrose as solute and H125, V5 and CC2 cylinders (see Table 6.15). It can be seen that D does not vary with Re (annulus) in a regular manner.

It should be noted that the experimental error was higher at the higher values of Re (annulus) for two reasons:-

(1) The flowrate pulsed much more at higher flowrates and so the apparent weight of the porous cylinder, which depends on flowrate, varied with time. This caused a waver on the recorder chart and an estimate of the mean curve had to be drawn in, after the run had finished.

(2) The higher flowrates made it more difficult to exclude air bubbles on the suction side of the pump. The bubbles sometimes reached the cylinder and so the certainty, that all weight changes were due to mass transfer, was reduced.

Conclusion External flow conditions do not influence the rate of mass transfer in porous media.

7.8. Effect of the Diameter of the Diffusing Particle

The diameter of the diffusing particle for the three systems investigated has been estimated (see Appendix 1). In Figs. 17 and 18 D and D^1 are plotted against d, the diameter of the diffusing particle, for absorption and desorption respectively. The values of D and D^1 are experimental values at levels r_2 c_2 a and r_2 c_2 d. Mean values were not plotted because the existence of interactions and dependence of D and D^1 on radius, concentration and method make them almost meaningless.

From Figs. 17 and 18 two conclusions can be drawn:-

(1) D and D^1 decrease with increase in d.

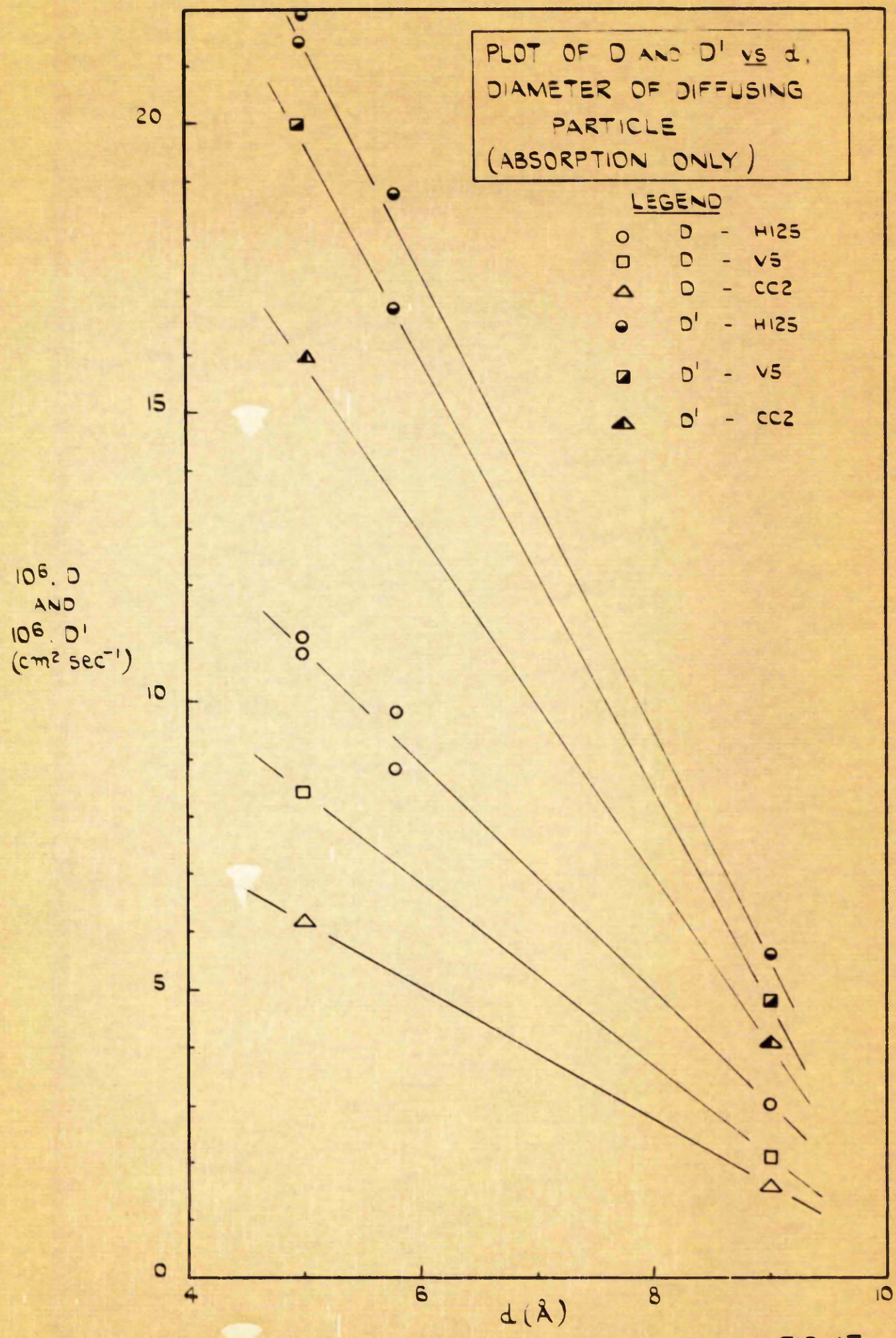
PLOT OF D AND D' vs d,
DIAMETER OF DIFFUSING
PARTICLE
(ABSORPTION ONLY)
LEGEND
D - H125
D - V5
D - CC2
D' - H125
D' - V5
D' - CC2
10^6. D
AND
10^6. D'
($cm^2\ sec^{-1}$)
0
5
10
15
20
4
6
8
10
d (Å)

FIG. 17.

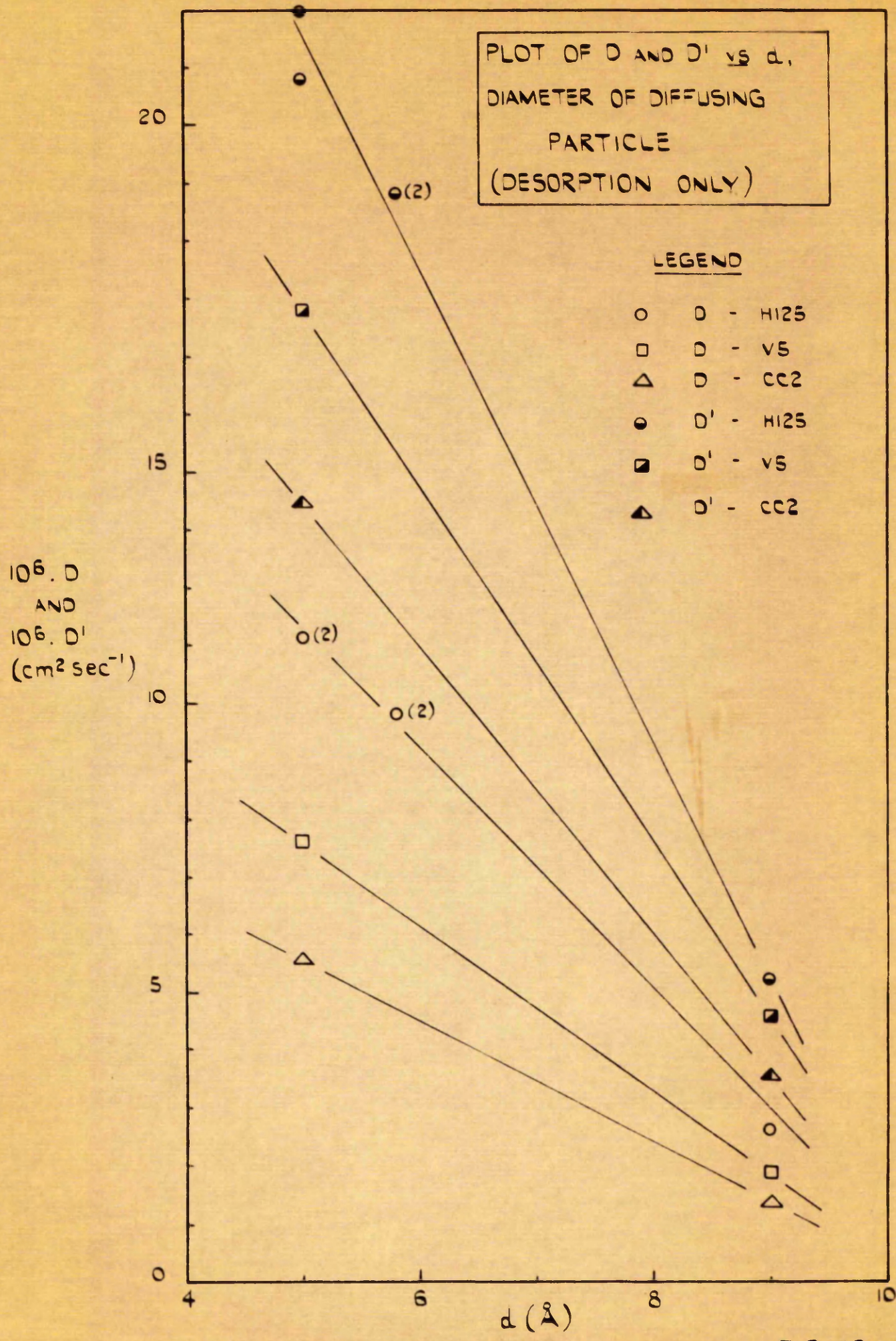
PLOT OF D AND D' VS d,
DIAMETER OF DIFFUSING
PARTICLE
(DESORPTION ONLY)
LEGEND
D - HI25
D - V5
D - CC2
D' - HI25
D' - V5
D' - CC2
O(2)
O(2)
O(2)
20
15
10
5
0
4
6
8
10
d (Å)
10⁶. D
AND
10⁶. D'
(cm² sec⁻¹)

FIG. 18.

(2) With H125 cylinders, when three solute-solvent systems were studied, D and D^1 decreased linearly with d, i.e. $D \propto - d$.

There is a high probability that this correlation is correct as repeats were carried out for both KCl-water and CCl_4-methanol and all the points fit the straight line well.

Comparing the variation with d of D in the H125 cylinders to D in free solution, the trend is the same but D in the H125 porous cylinders varies more linearly with d than D in free solution.

7.9 Effect of the Properties of the Porous Media

7.9.1. Comparative Values of K^2

The values of K^2 at nominal radius $r_2 = 0.65$ cm. are given in Table 6.16. The conclusions drawn from Table 6.16 are:-

(1) For all three porous materials, the value of K^2 for KCl is always greater than that for sucrose. For the H125 cylinders, the solutes in order of increasing K^2 (or degree of hindrance by porous media) are sucrose, carbon tetrachloride, potassium chloride, i.e. the larger the diffusing particle, the less it is hindered by the porous media.

(2) For sucrose and carbon tetrachloride, K^2 decreases as the initial solute concentration increases, but for potassium chloride K^2 increases as the initial solute concentration increases. A possible explanation is that adsorption of the solute molecules on the pore walls occurs. With the larger molecules (sucrose and, to a lesser degree, carbon tetrachloride,) the available pore wall area is limited and so, for concentrated solutions, no more molecules can be adsorbed and hence K^2 is smaller for concentrated solutions.

With potassium chloride molecules, more small molecules can be adsorbed (and the adsorption may be stronger than in the other cases, since it is an electrolyte) and the limit of the pore

wall area may not have been reached with 3N solutions. Thus, the more molecules in solution, the more would be adsorbed and K^2 would increase with concentration.

It must be noted, however, that K^2 is a ratio of two quantities which are not exactly comparable. D in free solution is the differential diffusivity measured at the stated concentration, D in the porous medium is the integral diffusivity measured in a range which starts at the stated concentration and would after infinite time, decrease to zero. Thus the trend in the values of K^2 is more important than the exact values.

(3) For sucrose and potassium chloride, K^2 is generally greater for desorption than absorption, i.e. desorption is the more hindered process. For carbon tetrachloride there is no appreciable difference between the values of K^2 for absorption and desorption.

7.9.2. Comparison of Values of K^2 and the Porosity Factor

Erdos and Jiru (27) stated that the value of K^2 (their symbol was Pd) was not dependent at all on the porosity of the porous medium. To test this statement, the quantity corresponding to K^2 was defined as the porosity factor, F_p.

$$F_p = \frac{100}{\text{mean porosity of porous medium}}$$

From Table 6.16, mean values of K^2 were calculated for each porous material and the mean values compared with the values of F_p.

Table 7.7. Comparative Values of K^2 and F_p

Porous Material	Mean Value of K^2	Mean Value of F_p
H125	1.62	1.95
V5	2.16	2.35
CC2	2.91	2.56

Although the values of K^2 and F_p are not the same, the experimental evidence indicates that K^2 is related to the porosity and so contradicts the statement of Erdos and Jiro.

Table 7.7 also shows that, excepting the CC2 cylinders, the value of F_p is greater than the value of K^2, i.e. the decrease in diffusivity is less than the decrease in available volume. This means that the reduction in surface area and the other factors which tend to reduce mass transfer are connected with the decrease in the available volume but are not directly proportional to it.

In connection with the porosity effect it was thought that if a correction for the porosity was made to the experimental values of D, the significance of other properties of the porous media would be clearly shown. For this reason values of $D' = \frac{D}{\text{individual cylinder porosity}}$ were tabulated and the results statistically analysed, and the conclusions compared with those of statistical analyses of the values of D.

The comparison was disappointing in as far as it did not give any new information (see Figs. 17-23, 25-28, 30) but merely emphasised the effect of variables, e.g. in the cases H125-sucrose-water, V5-sucrose-water, CC2-sucrose-water, the concentration c, the method m, and the method m respectively become significant at the 5% level for D' which were insignificant at the 5% level for D. In the case V5-KCl-water,

PLOT OF D vs P. MEAN POROSITY OF THE POROUS MEDIUM.

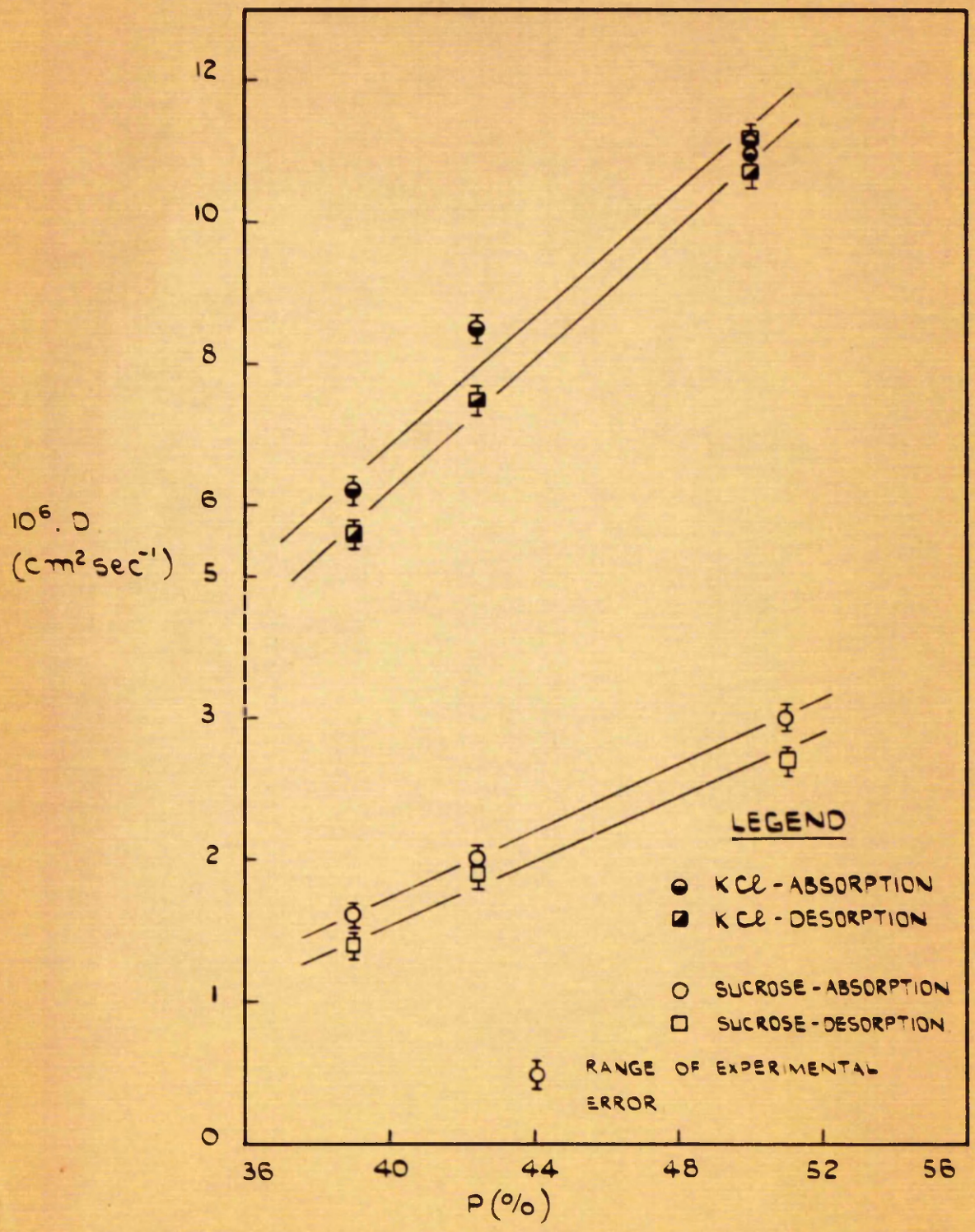

FIG. 24

PLOT OF D AND D' vs d.

MEAN PORE DIAMETER OF

POROUS MEDIUM (KCl RESULTS)

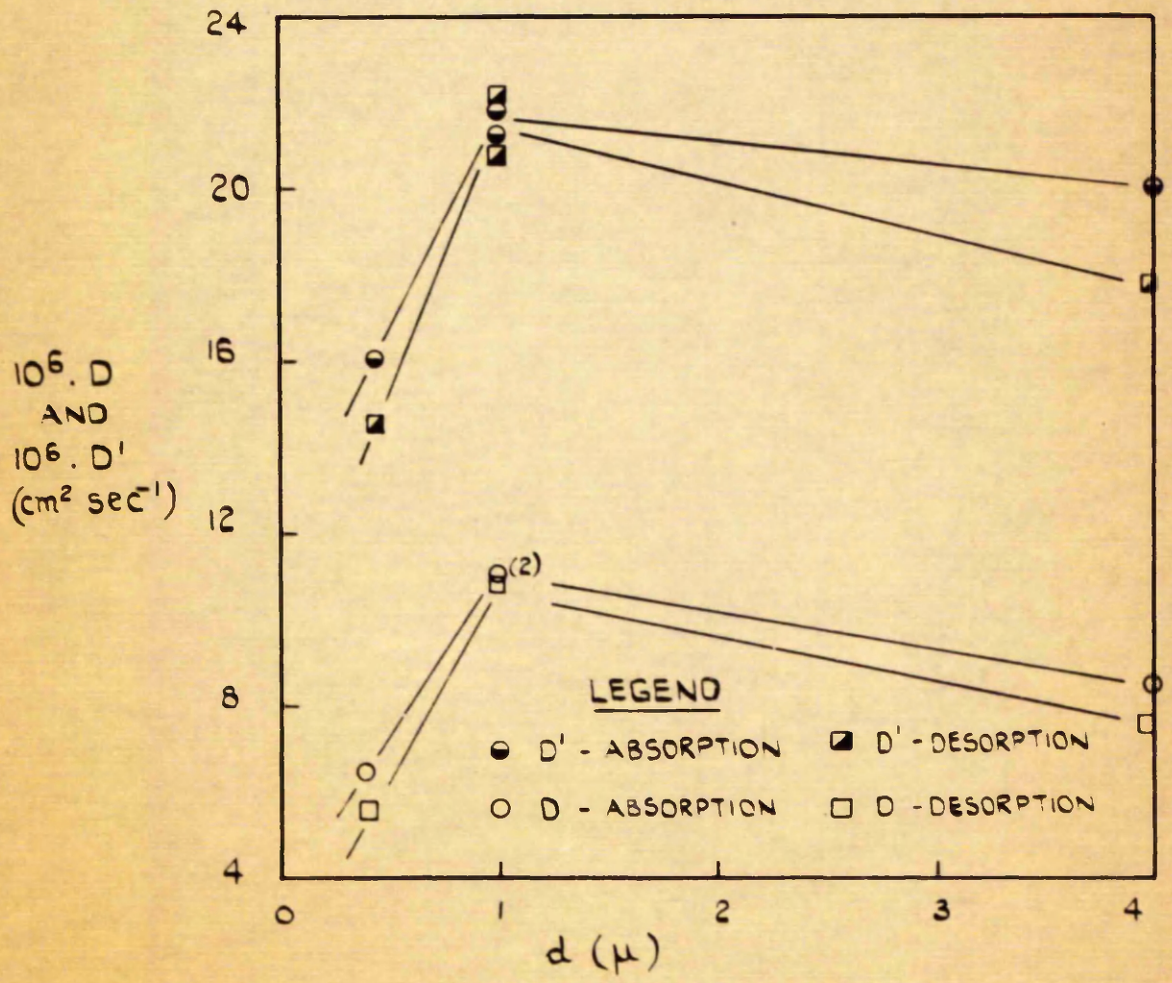

FIG 25

PLOT OF D AND D' vs d,
MEAN PORE DIAMETER OF
POROUS MEDIUM (SUCROSE RESULTS)

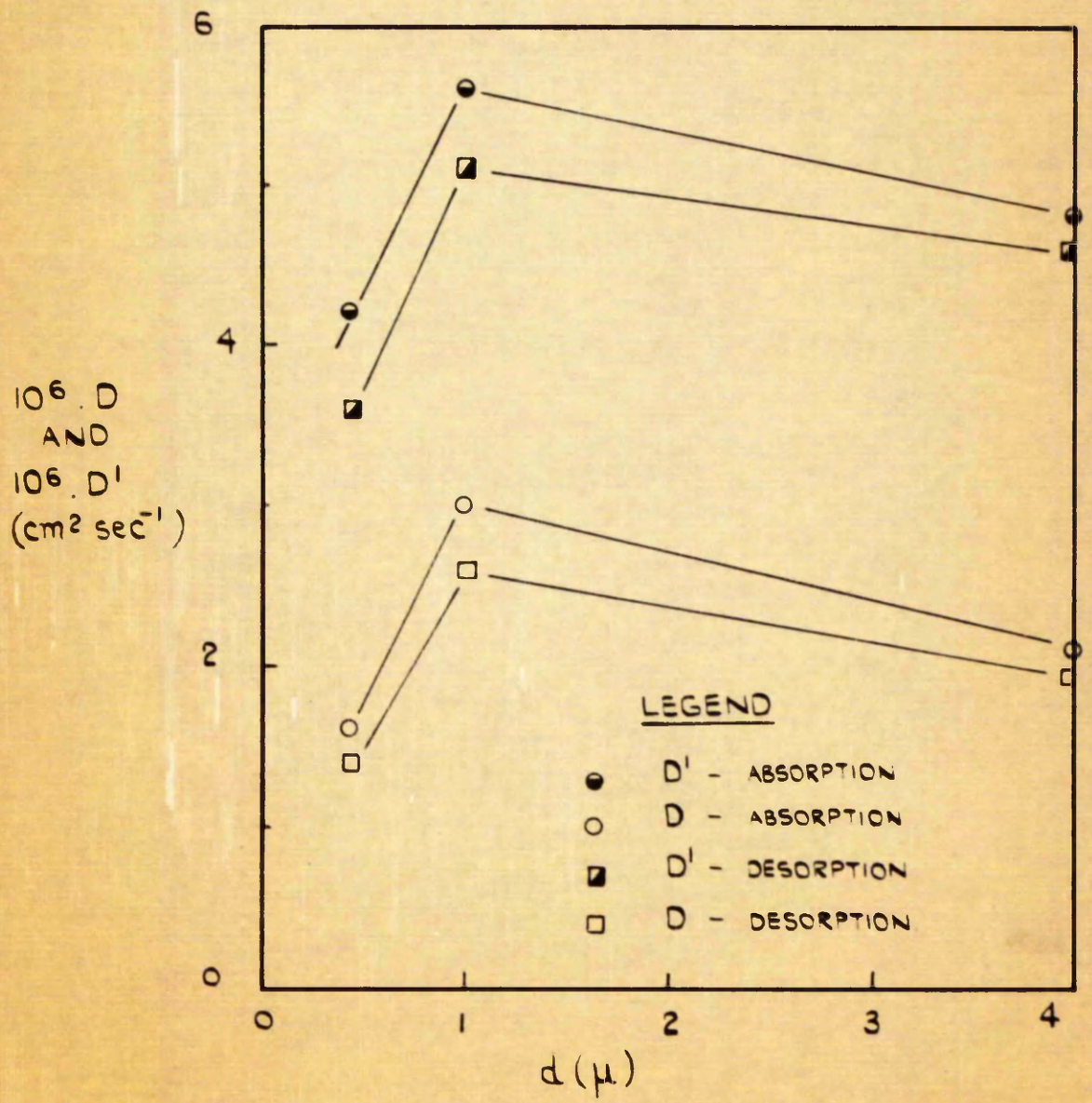

FIG. 26.

method m is significant at the 1% level for D^1 whereas it is only significant at the 5% level for D.

7.9.3. Effect of Particular Physical Properties of the Porous Media

7.9.3.1. Effect of Total Porosity

In the preceding sections the importance of the porosity of the porous medium has been emphasised.

From Fig. 24 it is clear that, within the experimental error, D is linearly proportional to P, the porosity, for KCl-water and sucrose-water.

7.9.3.2. Effect of Mean Pore Diameter

From Figs. 25 and 26 it can be seen that there is no correlation between D and the mean pore diameter.

7.9.3.3. Effect of Pore Entrance Size Distribution

As the criterion of pore entrance size distribution, the percentage of the pore volume composed of pores with diameter less than 1μ was taken. The choice was arbitrary but was considered to be a reasonable one.

From Figs. 27 and 28, it can be seen that any correlation between D and ϵ is completely masked by the porosity effect.

7.9.3.4. General Discussion of the Effects of the Physical Properties of the Porous Media

Fig. 24 indicates that D is linearly proportional to porosity but Table 6.24 suggests that the ratio of D for H125 and V5 cylinders is related to the square of the ratio of the porosity. As there is only one value of the porosity ratio and as the ratio of D^1 is only in slightly better agreement than the ratio of D, it is wiser to postulate that D is linearly related to the porosity.

PLOT OF D AND D' vs θ.

PERCENTAGE OF PORE VOLUME

LESS THAN 1μ PORE ENTRANCE

DIAMETER (KCl RESULTS)

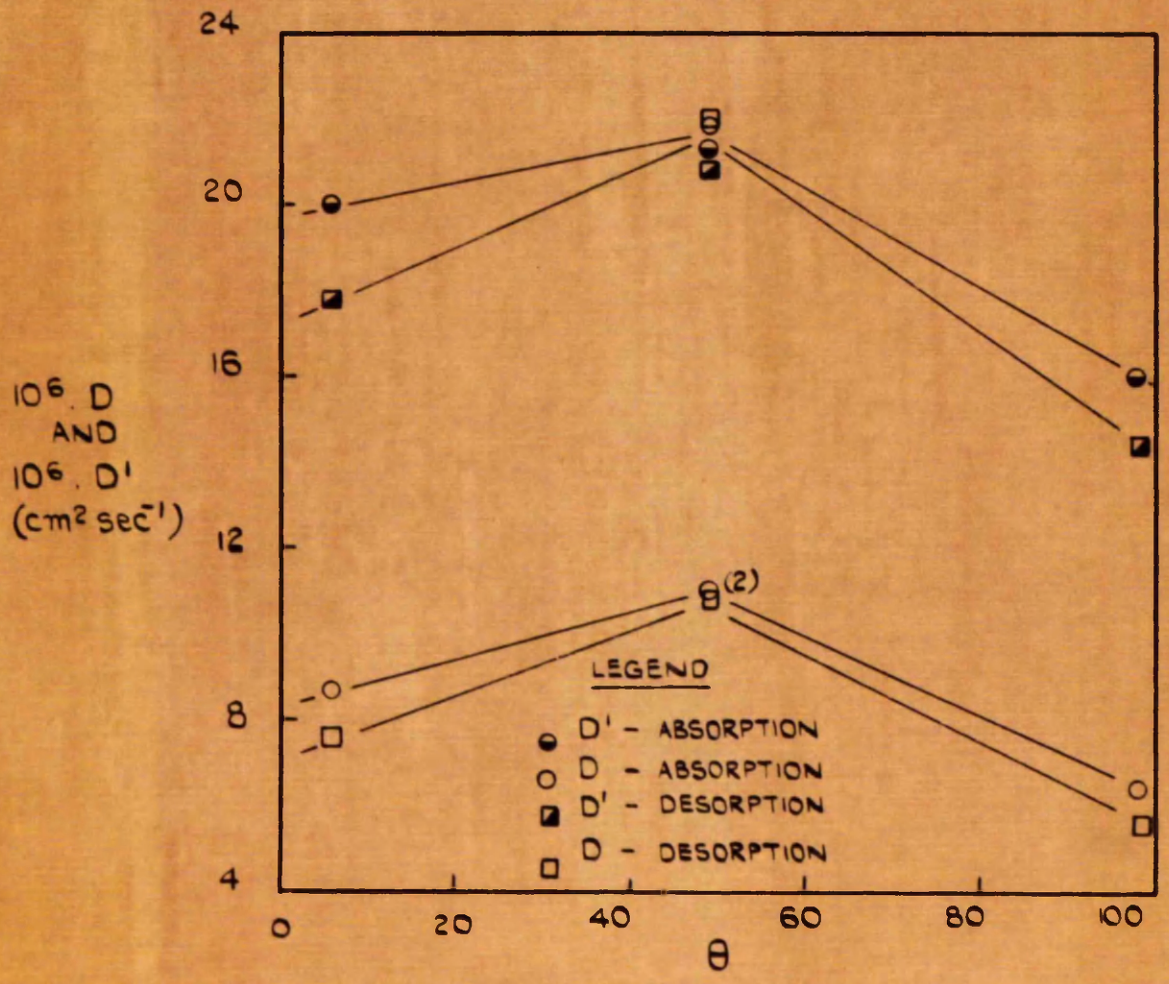

FIG. 27

PLOT OF D AND D' vs θ,
PERCENTAGE OF PORE VOLUME
LESS THAN 1μ PORE ENTRANCE
DIAMETER (SUCROSE RESULTS.)

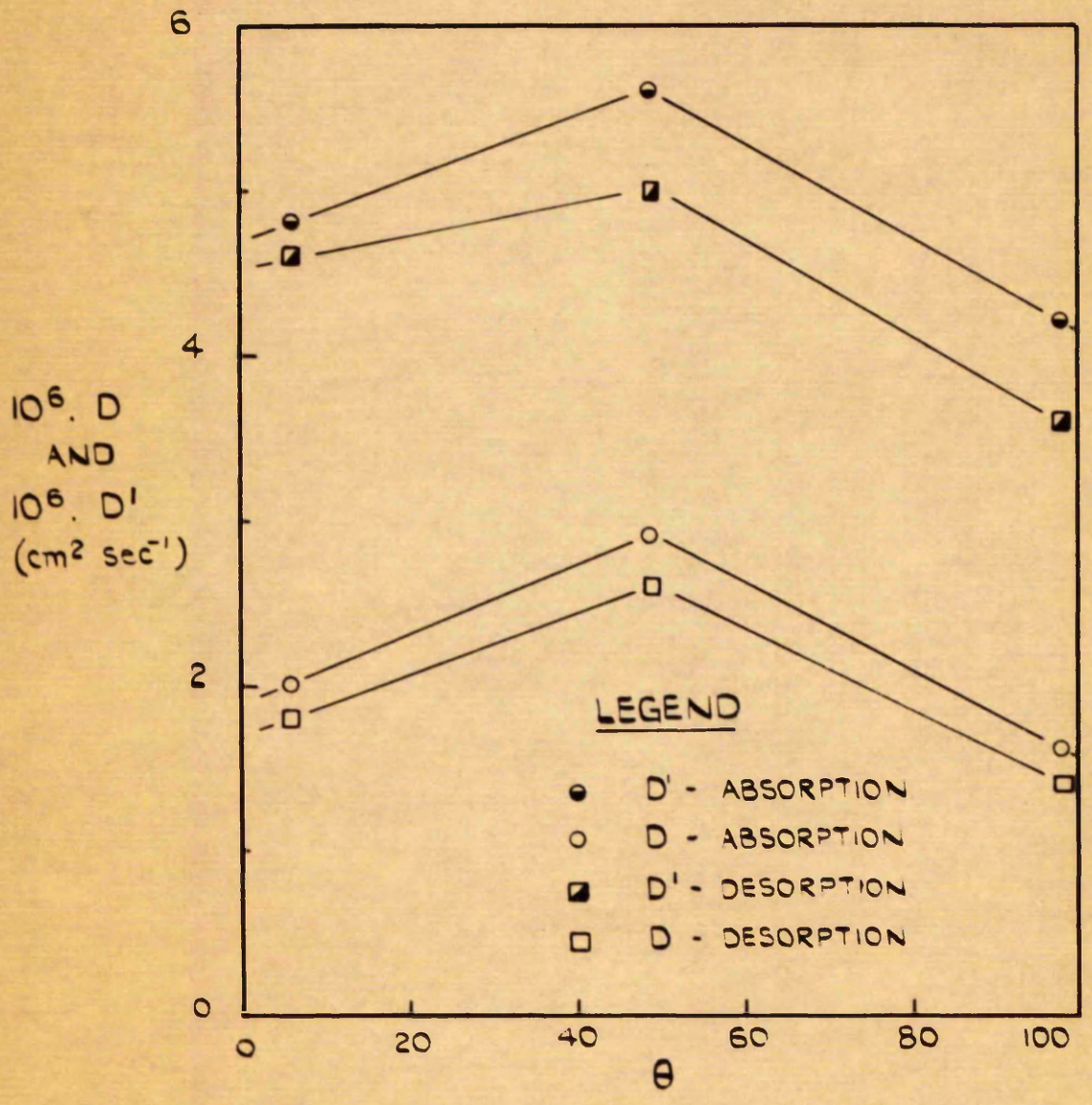

FIG 28

Table 6.24 indicates that, particularly for fine pore structures, D is a function of P, the percentage of the pore volume occupied by pores less than 1μ diameter.

Therefore the effects of the pore structure on D can be summarised by the formula:-

$$D = a + b\,(\text{Porosity}) + f\,(P)$$

where a and b are constants

$f(P)$ = function of (P)

7.10 Effect of the Interaction of the Diffusing Particle and the Porous Media

It has been suggested (45) that z, the ratio of the diameter of the diffusing particle to the mean pore diameter, was of primary importance in mass transfer in porous media. Figs. 29 and 30 show that there is no simple relationship valid for all porous materials. Fig. 29 indicates that the dependence of D on z is different for each porous material. From Figs. 30 it can be seen that the results for H125 and CC2 cylinders are slightly related but that the V5 results stand alone.

Therefore, for large pores, the ratio z has no effect on the value of D. Thus a tentative formula could be postulated:

$$D = f_1\,(\text{Porosity}) + f_2\,(P) + f_3\left(\frac{dp}{d}\right)$$

where $f_3\left(\frac{dp}{d}\right)$ is negligible for large pores

dp = diameter of diffusing particle

d = mean pore diameter of porous medium

Friedman & Kraemer (46) suggested the following relationship for mass transfer in gels.

$$D_s = D_g\left(1 + 2.4\,\frac{r}{R}\right)\ (1 + \alpha)\ (1 + \beta)$$

where D_s = diffusivity in free solution

D_g = diffusivity in gel

r = radius of diffusing particle

PLOT OF $\bar{D}$ vs Z,

RATIO $\frac{\text{DIAMETER OF DIFFUSING PARTICLE}}{\text{MEAN PORE DIAMETER}}$

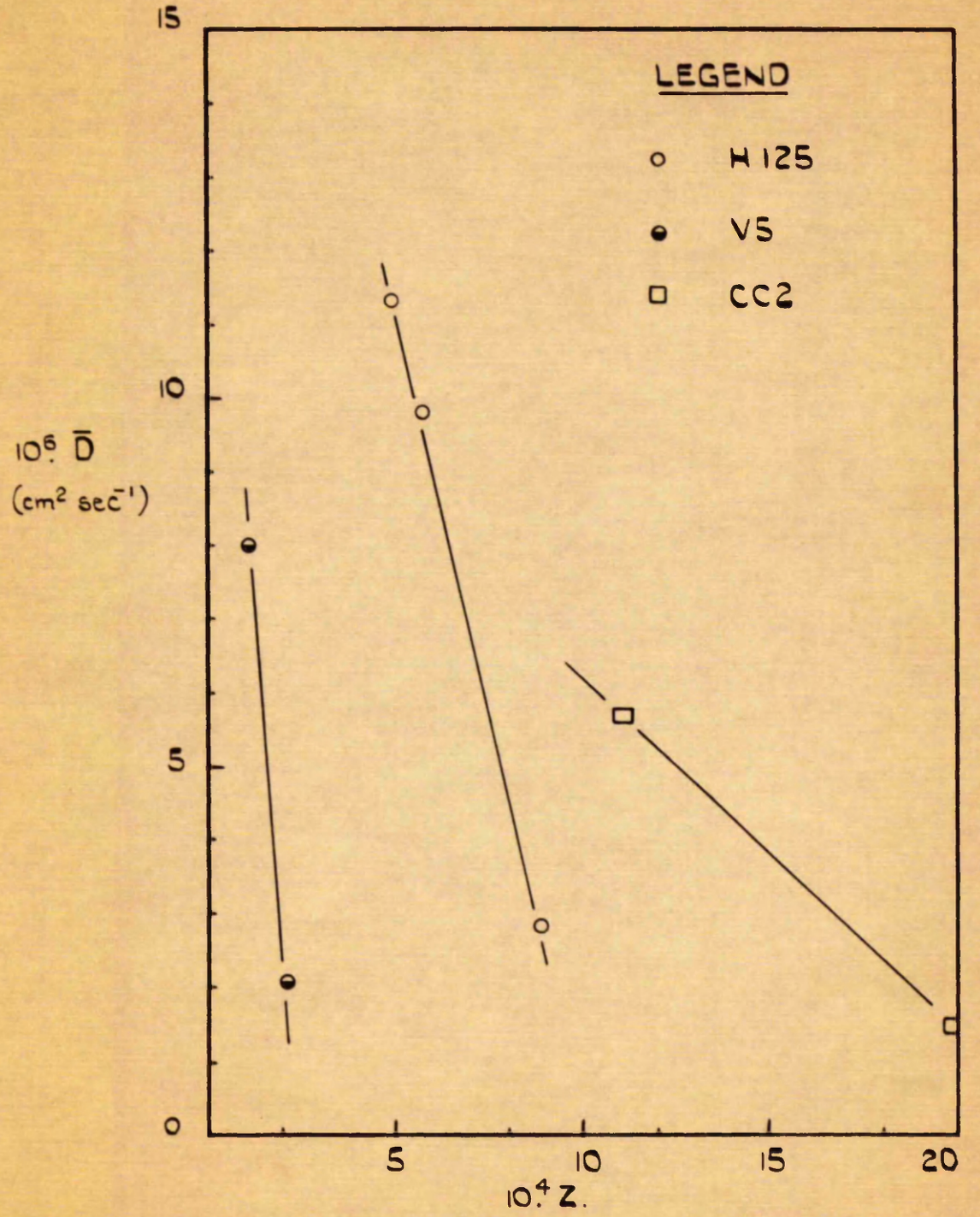

FIG 29.

PLOT OF D' vs Z.

RATIO $\frac{\text{DIAMETER OF DIFFUSING PARTICLE}}{\text{MEAN PORE DIAMETER}}$

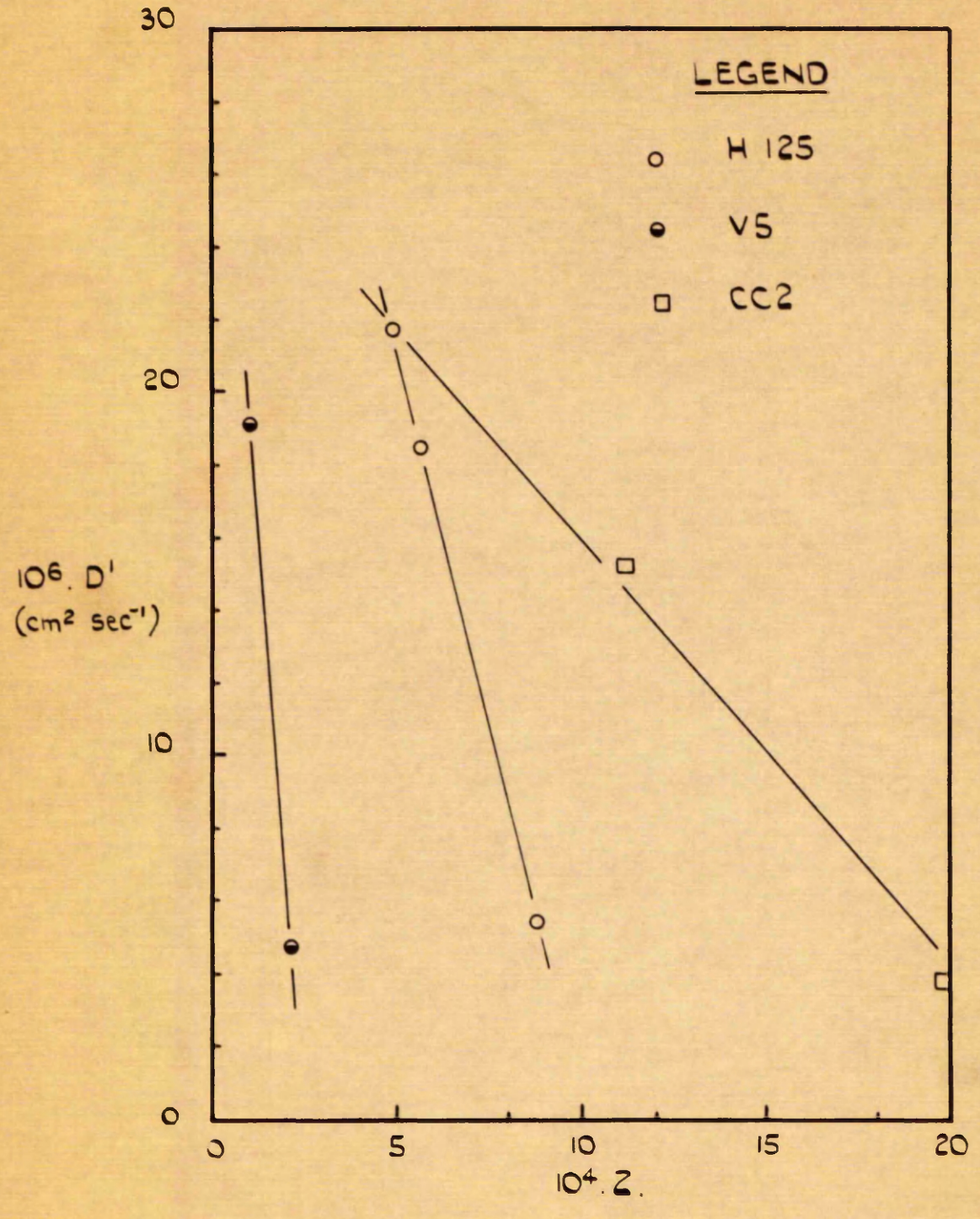

FIG. 30.

R = radius of the pores in the gel.

α = a correction factor for the difference in viscosity between the liquid in the gel and pure solvent.

β = a correction for the mechanical blocking effect.

The experimental values of D at the levels r_2 c_2 a and r_2 c_2 d were substituted into the above relationship and the results are given in Table 7.8. No figure for α was available and it was assumed zero. β was taken as $(1 - \frac{\text{porosity}}{100})$.

Table 7.8

Porous Material	Solute-Solvent System	10^6 D_s (experimental)	10^6 D_s (calculated)	% Error
H125	KCl-water	20.1	16.4	- 18
H125	Sucrose-water	3.2	4.15	+ 30
H125	CCl_4-methanol	15.0	14.5	- 3
V5	KCl-water	20.1	12.6	- 37
V5	Sucrose-water	3.2	3.15	- 2
CC2	KCl-water	20.1	9.5	- 51
CC2	Sucrose-water	3.2	2.4	- 24

It is obvious that in only two cases do the calculated values of the diffusivity in free solution agree with experiment.

Therefore the correlation does not appear to be valid for the systems studied.

Attempted Correlations

Starting with the simplest correlation, remembering that D is a function of porosity and P, the percentage of the pore volume filled by pores less than 1μ diameter, the following relationship was tried:-

$$D = a + b\,(\text{Porosity}) + c\,(P)$$

Using experimental values of D at the levels r_2 c_2 a and r_2 c_2 d, the values of the constants a, b, c were:-

D = - 8.02 + 0.390 (porosity) - 0.006 (P) - KCl - water

D = - 2.19 + 0.099 (porosity) - 0.002 (P) - sucrose - water

Obviously the form of the correlation is not that to give a correlation of general applicability.

The following correlation was then tried:-

$$D_f = D_e \frac{1 + a P}{1 + b\ (\text{porosity})}$$

where D_f = diffusivity in free solution.

D_e = experimental diffusivity.

When the values of D for H125 and CC2 cylinders at levels r_2 c_2 a and r_2 c_2 d were substituted into the relationship, the values of the constants a and b were:-

a = 0.0325; b = 0.0245 sucrose-water

a = 0.0480; b = 0.0170 KCl-water

Thus there is no simple algebraic relationship which correlates the results for all systems, and the most satisfactory formula is that given in 7.9.3.4., namely

D = a + b (porosity) + f (P)

---

8. CONCLUSIONS

1. Experiments were carried out in the form of planned statistical series. Duplicate runs were carried out and the probability of an effect was measured statistically and confidence limits given.

2. Two experimental methods of measuring the diffusivity of potassium chloride in water gave results which agreed to within 4%.

3. The percentage experimental error of experiments using the recording balance is 0.8 - 1.4%.

4. (a) For aqueous solutions absorption occurs more quickly than desorption; for organic solutions desorption occurs more quickly than absorption.

   (b) For aqueous solutions the method of sorption becomes statistically more significant as the porosity of the porous medium decreases.

   (c) Experimental data for the systems, potassium chloride-water and carbon tetrachloride-methanol agree with the theoretical prediction of Crank and Henry regarding the relative rates of absorption and desorption. The experimental data for the sucrose-water system does not agree with their prediction.

5. The diffusivity in porous media varies with initial solute concentration in the same way as does the diffusivity in free solution.

D for potassium chloride-water increases slightly as the initial solute concentration increases; D for sucrose-water decreases as the initial solute concentration increases.

6. The effect of cylinder radius r on the diffusivity, D, depends on the grade of the porous medium.

   For H125 porous cylinders, D does not vary with radius; for V5 and CC2 porous cylinders, D increases slightly as r increases.

7. External flow conditions have no effect on the diffusivity in the porous media examined.

8. Diffusivity decreases as the diameter of the diffusing particle, d, increases. For H125 cylinders D decreases approximately linearly with d.

9. (a) The larger the diffusing particle, the less it is hindered by the porous material. For H125 cylinders, the solutes in order of increasing degree of hindrance are sucrose, carbon tetrachloride, potassium chloride.

   (b) The degree of hindrance to diffusion is related to the porosity of the porous medium.

   (c) The mean pore diameter and the pore size distribution parameters had a small effect on the diffusivity. The chief factor was the total porosity of the porous medium.

10. The experimental data does not indicate that D is dependent on the ratio of the diameter of the diffusing particle to the mean pore diameter of the porous medium.

APPENDIX 1

SOLUTION OF THE DIFFUSION EQUATION

For cylindrical co-ordinates the differential equation is:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right)$$

assuming D is independent of concentration.

with the boundary conditions

(i) c finite as $t \longrightarrow + \infty$

(ii) c finite as $r \longrightarrow o$

(iii) $c = o$, at $r = a$ $(o < t < + \infty)$

(iv) $c = c_1$ at $t = o$ $(o < r < a)$

Let $c = R(r)\ T(t)$

$$\therefore R \frac{dT}{dt} = D \left[\frac{d^2 R}{dr^2} T + \frac{1}{r} \frac{dR}{dr} T \right]$$

$$\therefore \frac{1}{DT} \cdot \frac{dT}{dt} = \frac{1}{R} \left[\frac{d^2 R}{dr^2} + \frac{1}{r} \frac{dR}{dr} \right]$$

$$= \text{a constant}$$

Since the left hand side is a function of t alone and the right hand side is a function of r alone.

Put $- p^2 = \text{constant}$

$$\therefore \frac{1}{DT} \frac{dT}{dt} = - p^2$$

$$\therefore \frac{dT}{T} = - D p^2 dt$$

$\therefore$ $\ln T = - D p^2 t + \text{constant}$

$\therefore$ $T = A e^{- p^2 D t}$

$$\frac{d^2 R}{dr^2} + \frac{1}{r} \frac{dR}{dr} + p^2 R = 0$$

$\therefore$ $R = B\, Jo\,(pr) + C\, Yo\,(pr)$

where B and C are constants

Jo (pr) = Bessel function at zero order

Yo (pr) = Weber's Bessel Function of zero order

$\therefore$ $C = e^{-p^2 D t} [B^1 Jo\,(pr) + C^1 Yo\,(pr)]$

If we put the constant = o

then T = A

and R = C + B log r

$\therefore$ C = A + B log r

$\therefore$ the most general solution is

$C = A + B \log r + e^{-p^2 D t} [B^1 Jo\,(pr) + C^1 Yo\,(pr)]$

C is finite as $r \longrightarrow o$ and $t \longrightarrow + \infty$

$\therefore$ $B = o$ and $C^1 = o$

$\therefore$ $C = e^{-p^2 D t} B^1 Jo\,(pr)$

condition (iii) gives

$o = e^{-p^2 D t} B^1 Jo\,(pa)$

$\therefore$ $Jo\,(pa) = o$

$\therefore$ $pa = \alpha_s$, a typical root of $J0\,(\alpha) = o$

$\therefore$ $c = B^1 e^{- \frac{D \alpha_s^2 t}{a^2}} Jo\left(\frac{\alpha_s}{a} r\right)$

Taking a series solution

$$C = \sum_{s=1}^{\infty} A_s \; e^{- \frac{D \alpha_s^2 t}{a^2}} \; Jo \left(\frac{\alpha_s}{a} r \right)$$ and putting

$$x = r/a$$

when condition (iv) is applied

$$C_1 = \sum_{s=1}^{\infty} A_s \, Jo \, (\alpha_s x) \quad (o < x < 1)$$

$$\therefore \quad A_s = \frac{2}{J_1^{\,2} (\alpha_s)} \int_o^1 x \, C_1 \, Jo \, (\alpha_s x) \, d x$$

$$= \frac{2 C_1}{J_1^{\,2} (\alpha_s)} \left[\frac{1}{\alpha_s} x \, J_1 \, (\alpha_s x) \right]_o^1$$

$$= \frac{2 C_1}{\alpha_s \, J_1 \, (\alpha_s)}$$

$$\therefore \quad C = 2 C_1 \sum_{s=1}^{\infty} \frac{1}{\alpha_s \, J_1 \, (\alpha_s)} \; Jo \left(\frac{\alpha_s}{a} r \right) \; e^{- \frac{D t \alpha_s^{\,2}}{a^2}}$$

A P P E N D I X 2

PROPERTIES OF THE SOLUTE-SOLVENT SYSTEMS

The properties considered relevant to diffusion in porous media are the integral mutual diffusivity in free solution, the diameter of the diffusing particle, and the value of 1/k (see 5.3).

These properties are now considered in turn.

1. Integral Mutual Diffusivity in Free Solution

Tabulated values of the mutual diffusivity are given below, together with the experimental method used and source of the information.

Table 1: Diffusivity in Free Solution of Potassium Chloride in Water (25°C.)

Concentration (gm.equiv./litre)	10^5 Diffusivity (cm^2/sec.)	Experimental Method	Source of Information
1	1.88	Magnetically-stirred porous diaphragm cell	(47)
2	2.01		
3	2.11		

Table 2: Diffusivity in Free Solution of Sucrose in Water (25°C.)

Concentration (weight %)	10^5 Diffusivity ($cm^2/sec.$)	Experimental Method	Source of Information
0.7 15.0 30.0 61.05	0.517 0.420 0.320 0.107	Schlieren concentration gradients measured by refractive index polarisation interferometer.	(34) (48) (49)
5.25	0.482	Gouy interference	(35)

Table 3: Diffusivity in Free Solution of Carbon Tetrachloride in Methanol (25°C.)

Concentration (weight %)	10^5 Diffusivity ($cm^2/sec.$)	Experimental Method	Source of Information
40 50 60	1.66 1.50 1.34	Magnetically-stirred porous diaphragm cell.	(53)

2. Size of the Diffusing Particle

Table 4: Diameters of the Diffusing Particles

Substance	Diameter of Diffusing Particle (Å)	Source of Information
Potassium Chloride	5.0	(51)
Carbon Tetrachloride	5.8	(52)
Sucrose	9.0	A scale model of sucrose

Notes: A scale model was used by the author to determine the largest dimension of a sucrose molecule. This depends on the relative configuration of the glucose rings.

The effective diameters of the diffusing particles in the case of potassium chloride and carbon tetrachloride were determined using data on ionic radii.

It was assumed that the volumes of the ions were additive and thus an effective diameter was calculated. In the case of potassium chloride 0.9 molecules of bound water per molecule of solute were included in the diffusing particle. This figure (the hydration number) was the empirical value found from diffusion data (51).

3. Values of 1/k

In section 5.3. it was shown that the analysis of the data obtained from the recording balance depended on the existence of a substantially linear relationship between solute concentration and the density of the solution, i.e.

$$p = p_o + k. C$$

Values of 1/k for the systems studied are given in Table 5.

Table 5

Solute-Solvent System	Temperature (°C.)	1/k	Source of Information
KCl-water	20	1.656	(53)
KCl-water	25	1.672	
KCl-water	30	1.696	
Sucrose-water	20	2.664	(54)
Sucrose-water	25	2.671	
Sucrose-water	30	2.677	
Sucrose-water	40	2.685	
CCl_4-methanol	25	1.981	(55)

Tables of concentration and density at 25°C. are given below. A specimen calculation of 1/k is also given.

Table 6: Density and Concentration Table (KCl-water)

x Concentration (gm. ml.$^{-1}$)	Y Density (gm. ml.$^{-1}$)
0.038	1.023
0.062	1.035
0.084	1.048
0.107	1.062
0.131	1.075
0.154	1.089
0.178	1.102
0.201	1.116
0.224	1.131

Table 7: Density and Concentration Table (Sucrose-water)

x Concentration (gm. ml.$^{-1}$)	Y Density (gm. ml.$^{-1}$)
0.0	0.997
0.051	1.017
0.104	1.037
0.159	1.058
0.216	1.079
0.275	1.102
0.338	1.125
0.402	1.149
0.470	1.174
0.540	1.200
0.614	1.227
0.690	1.255
0.770	1.284
0.854	1.314

Specimen Calculation

k is the slope of the plot of density vs concentration

$$\therefore \quad k = \frac{\Sigma x Y - a \Sigma x}{\Sigma x^2}$$

where a = density of water at 25°C.

= 0.997 gm. ml^{-1}

$$\therefore \quad k = \frac{6.636 - 0.997 \times 5.483}{3.125}$$

$$\therefore \quad k = 0.3744$$

$$\therefore \quad \frac{1}{k} = 2.671$$

APPENDIX 3

PROPERTIES OF THE POROUS MEDIA

The following properties of the porous media were determined experimentally:- bulk volume, pore volume and pore size distribution. Four porous materials were used - three grades of alumina-silicates and one grade of Teflon. The properties of the porous media are now considered in more detail.

1. Dimensions, Bulk Volume, Pore Volume and Porosity

The values of the square of the radius, the bulk volume, pore volume and porosity are given in Table 8.

Table 8: Physical Characteristics of the Porous Cylinders

Table 8a: Grade H125 (series 1) Nominal Length 2 ins.

Cylinder No.	Radius Group	$(\text{Radius})^2$ (cm^2)	Pore Volume (cm^3)	Bulk Volume (cm^3)	Porosity (%)
1	r_1	0.5949	4.78	9.49	50.4
4	r_1	0.6014	4.86	9.59	50.6
1	r_2	0.4282	3.55	6.83	51.9
3	r_2	0.4420	3.54	7.05	50.2
1	r_3	0.2601	1.96	4.15	47.1
11	r_3	0.2521	1.92	4.02	47.8

Table 8b: Grade H125 (Series 2) Nominal Length 3 ins.

Cylinder No.	Radius Group	(Radius)^2 (cm^2)	Pore Volume (cm^3)	Bulk Volume (cm^3)	Porosity (%)
1	r_1	0.5812	6.90	13.45	51.3
2	r_1	0.6021	7.247	14.184	51.1
1	r_2	0.4274	5.15	9.90	52.0
2	r_2	0.4177	5.092	9.840	51.7
1	r_3	0.2797	3.36	6.47	51.9
2	r_3	0.2626	2.20	4.33	50.8
4	r_3	0.2683	2.15	4.20	51.2
6	r_3	0.2770	2.17	4.28	50.7

Table 8c: Grade V5 Nominal Length 3 ins.

Cylinder No.	Radius Group	(Radius)^2 (cm^2)	Pore Volume (cm^3)	Bulk Volume (cm^3)	Porosity (%)
1	r_1	0.5805	5.76	13.67	42.1
1	r_2	0.4121	4.11	9.70	42.4
1	r_3	0.2572	2.61	6.06	43.1

Table 8d: Grade CC2 Nominal Length 3 ins.

Cylinder No.	Radius Group	(Radius)^2 (cm^2)	Pore Volume (cm^3)	Bulk Volume (cm^3)	Porosity (%)
1	r_2	0.4008	3.63	9.44	38.5
1	r_3	0.2676	2.36	6.30	37.5
2	r_3	0.2686	1.64	4.15	39.5
4	r_3	0.2630	1.67	4.13	40.4

Table 8e: Grade Teflon. Nominal Length 3 ins.

Cylinder No.	Radius Group	(Radius)^2 (cm^2)	Pore Volume (cm^3)	Bulk Volume (cm^3)	Porosity (%)
4	r_3	0.2600	1.39	4.05	34.5
8	r_3	0.2500	1.56	4.08	38.2
2	r_4	0.1440	0.87	2.31	37.8
5	r_4	0.1370	0.82	2.38	34.5

2. Pore Size Distribution

The results of the mercury porosimeter tests are presented graphically in two ways:-

(a) Cumulative volume occupied against pore entrance diameter which gives an S-shaped curve.

(b) Volume occupied against pore entrance which gives a "normal" curve from which the mean pore entrance diameter can be determined.

The results are shown graphically in Figs. 31 - 34 and a sample calculation is given below.

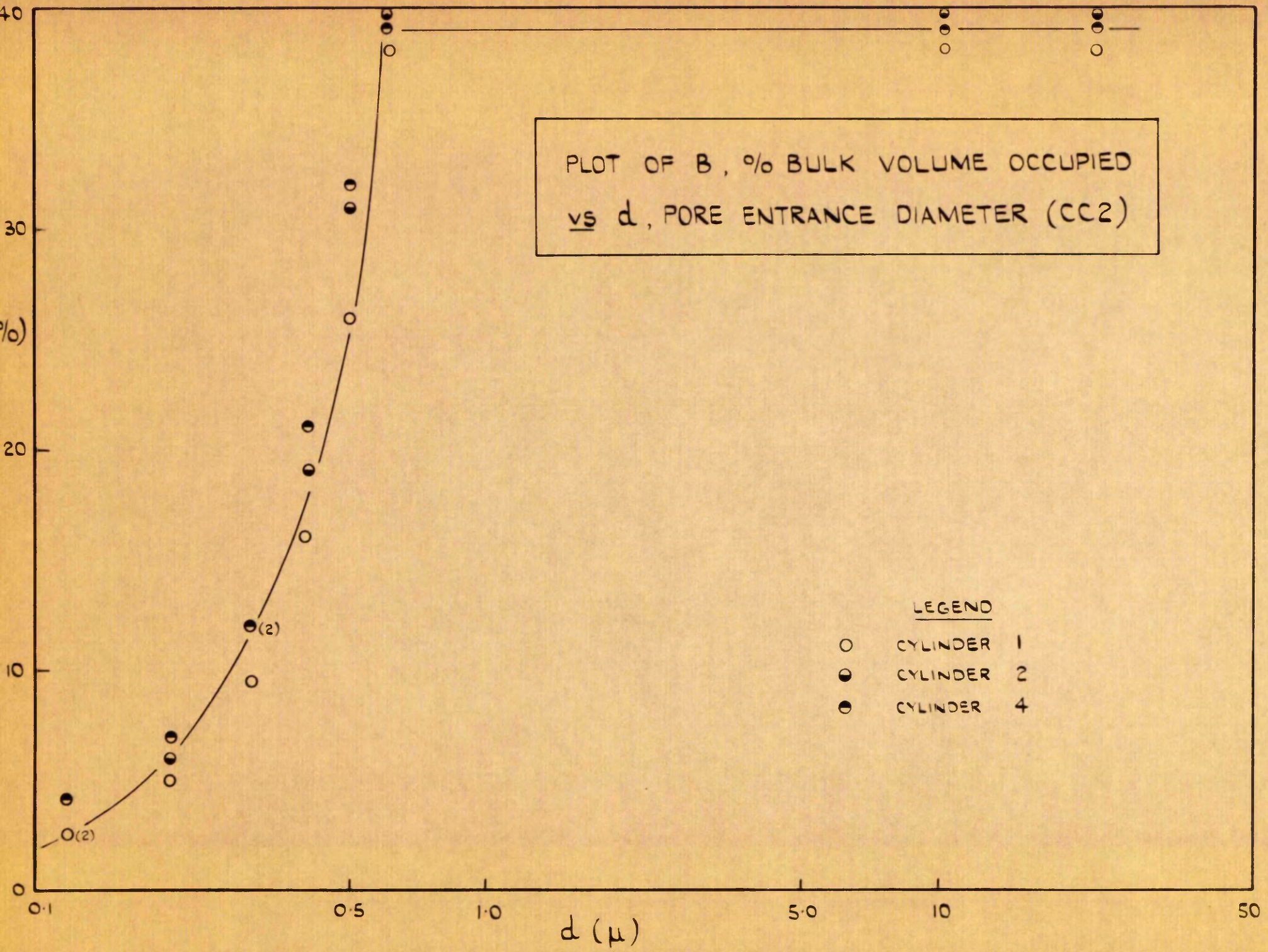
PLOT OF B, % BULK VOLUME OCCUPIED
vs d, PORE ENTRANCE DIAMETER (CC2)
LEGEND
CYLINDER 1
CYLINDER 2
CYLINDER 4
40
30
20
10
0
%)
0·1
0·5
1·0
5·0
10
50
d (μ)
(2)
(2)

FIG. 31d

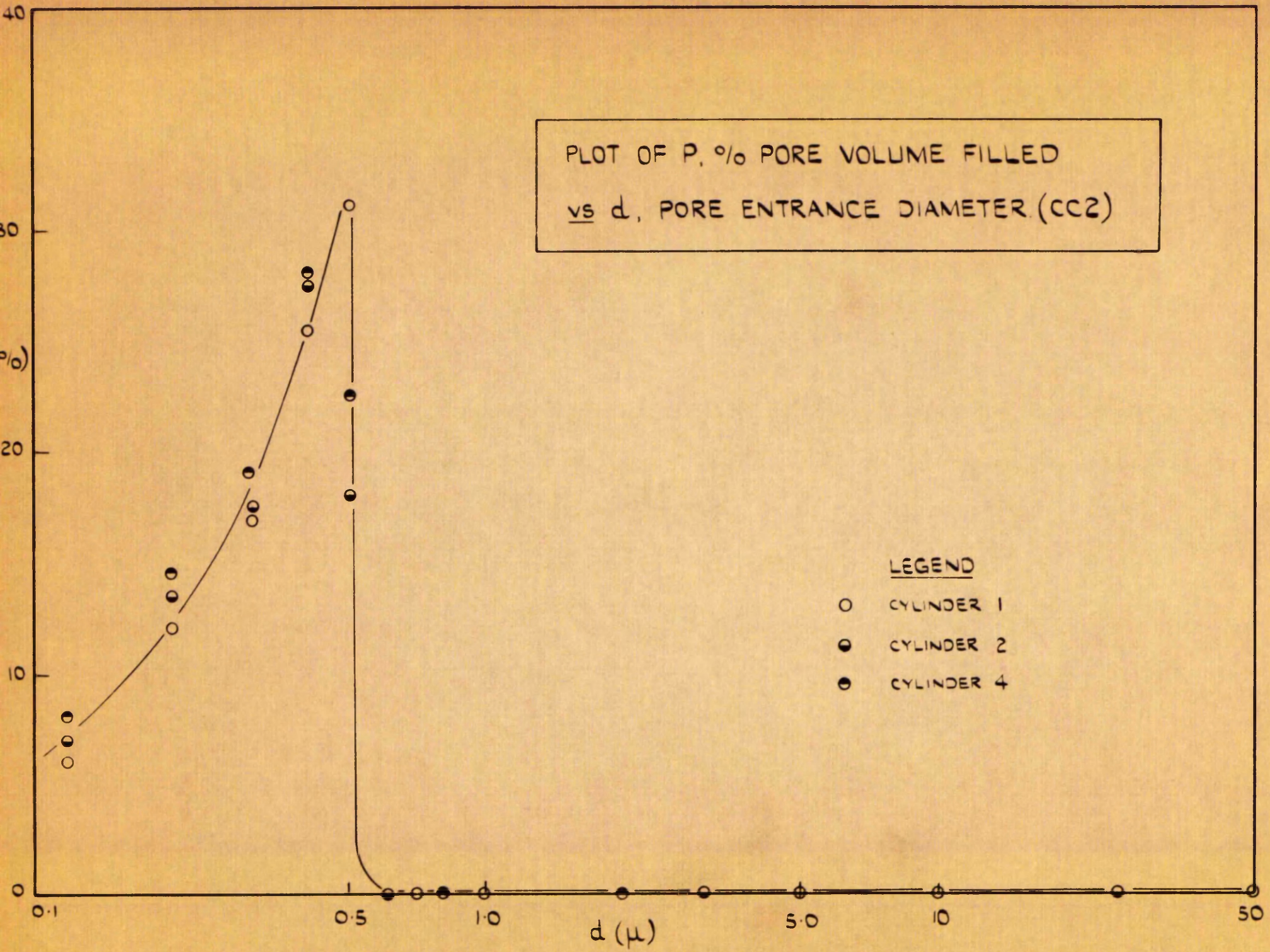
PLOT OF P, % PORE VOLUME FILLED
vs d, PORE ENTRANCE DIAMETER (CC2)
LEGEND
CYLINDER 1
CYLINDER 2
CYLINDER 4
40
30
20
10
0
P/o)
0·1
0·5
1·0
5·0
10
50
d (μ)

FIG. 31 b

PLOT OF B, % BULK VOLUME OCCUPIED

vs d, PORE ENTRANCE DIAMETER (H125)

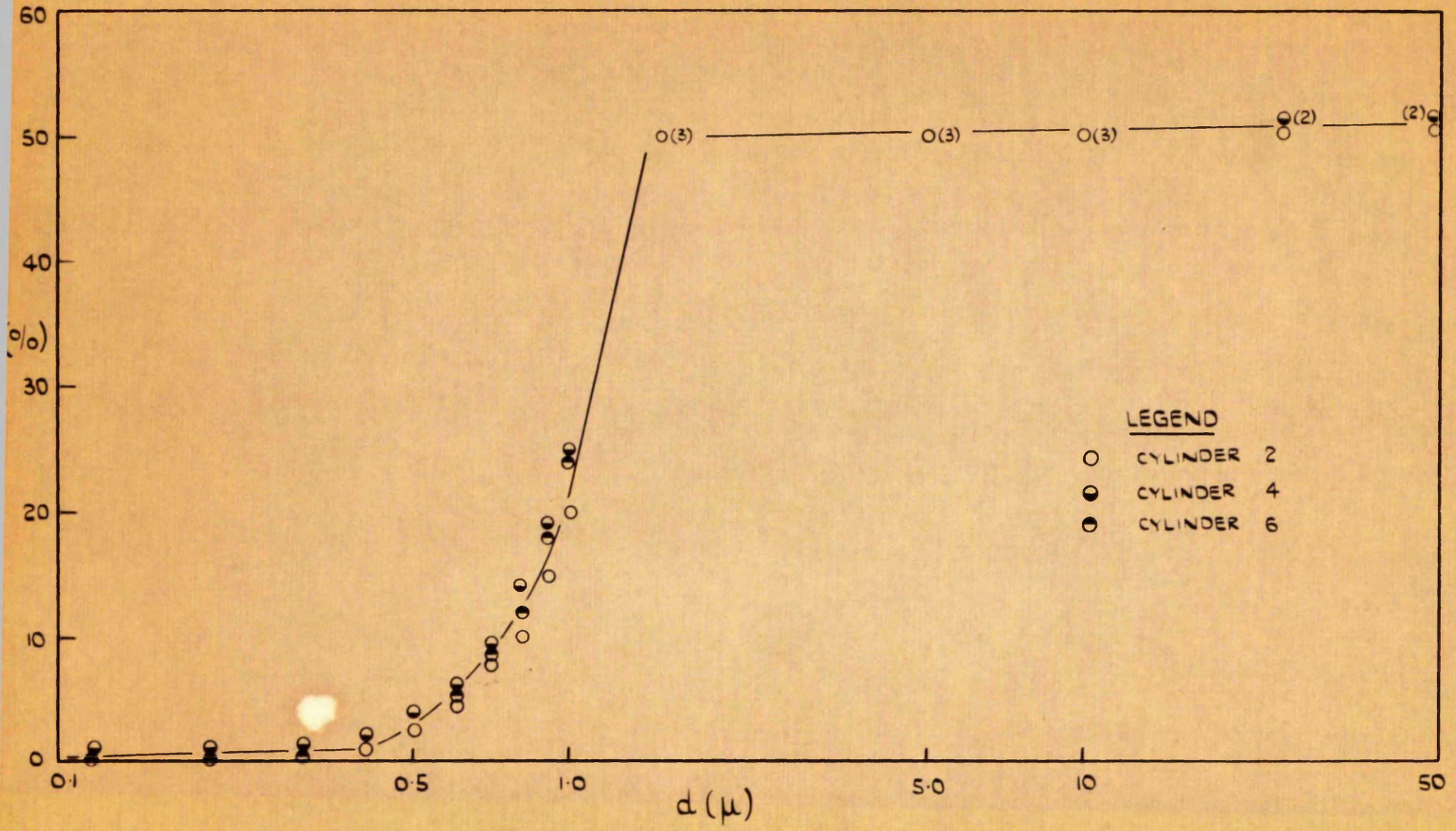

FIG 32 d

PLOT OF P, % PORE VOLUME FILLED

vs d, PORE ENTRANCE DIAMETER (H125)

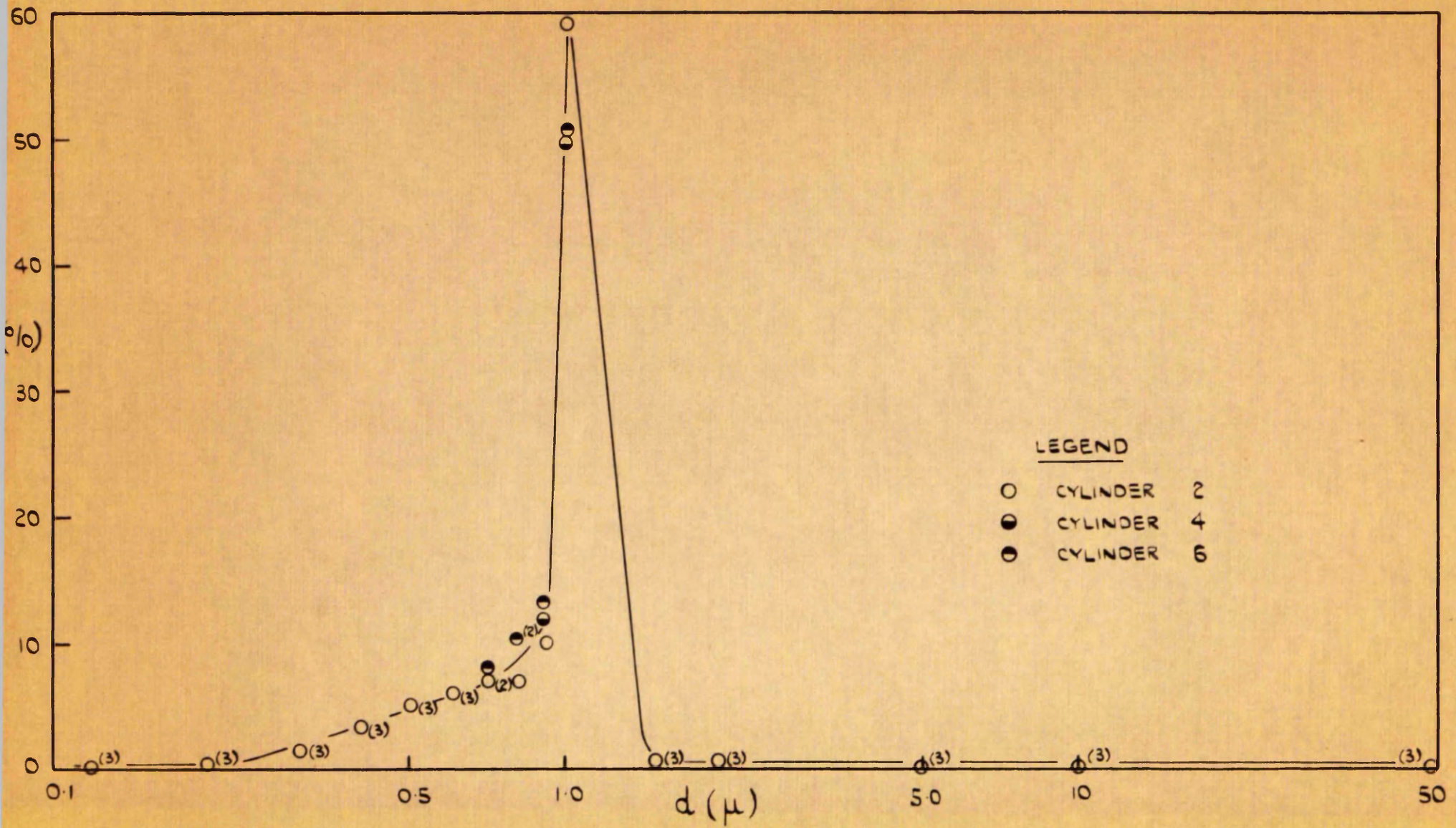

FIG 32 b

PLOT OF B, % BULK VOLUME OCCUPIED

vs d, PORE ENTRANCE DIAMETER (V5)

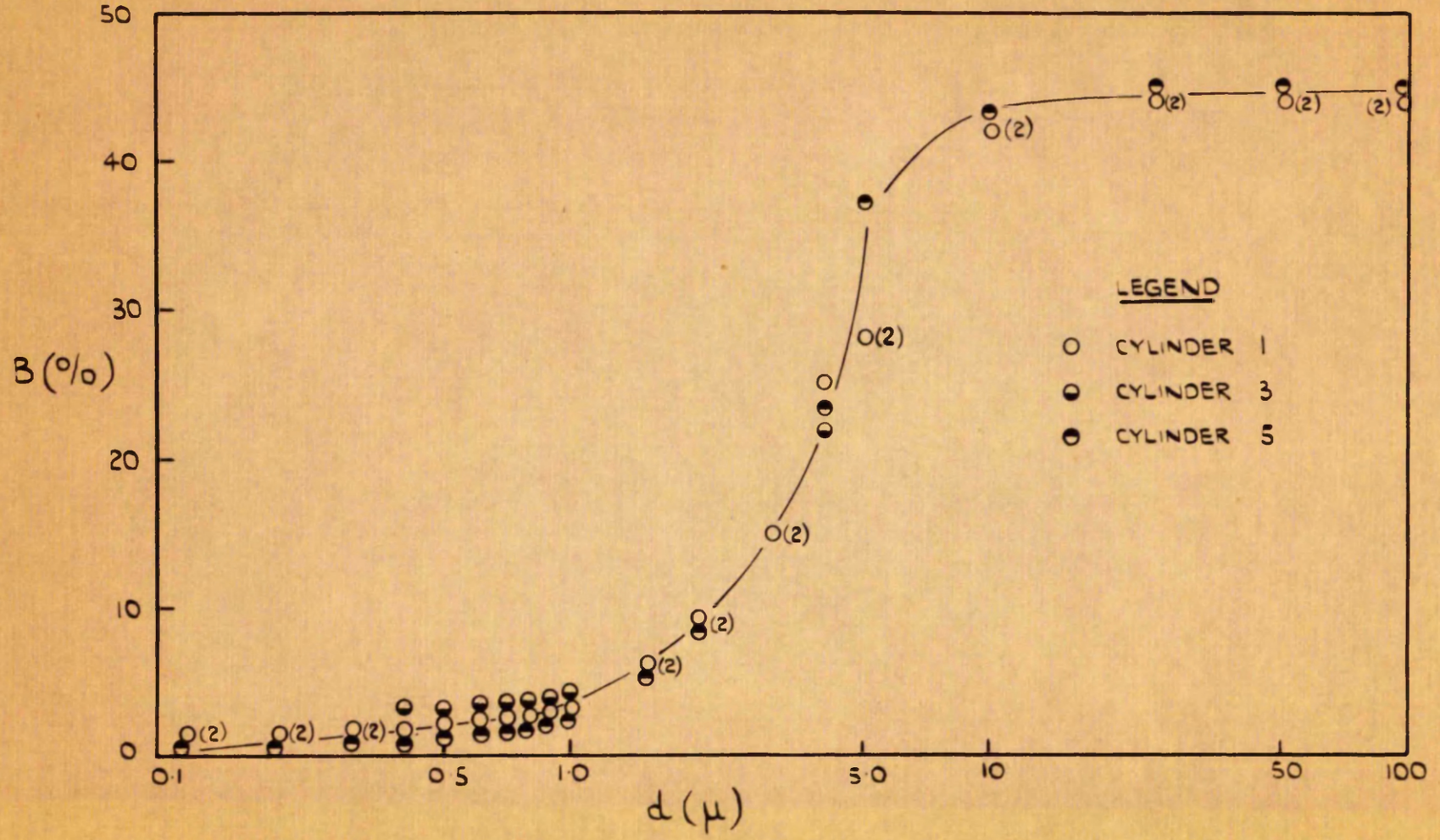

FIG. 33d.

PLOT OF P, % PORE VOLUME FILLED,

VS d, PORE ENTRANCE DIAMETER (VS)

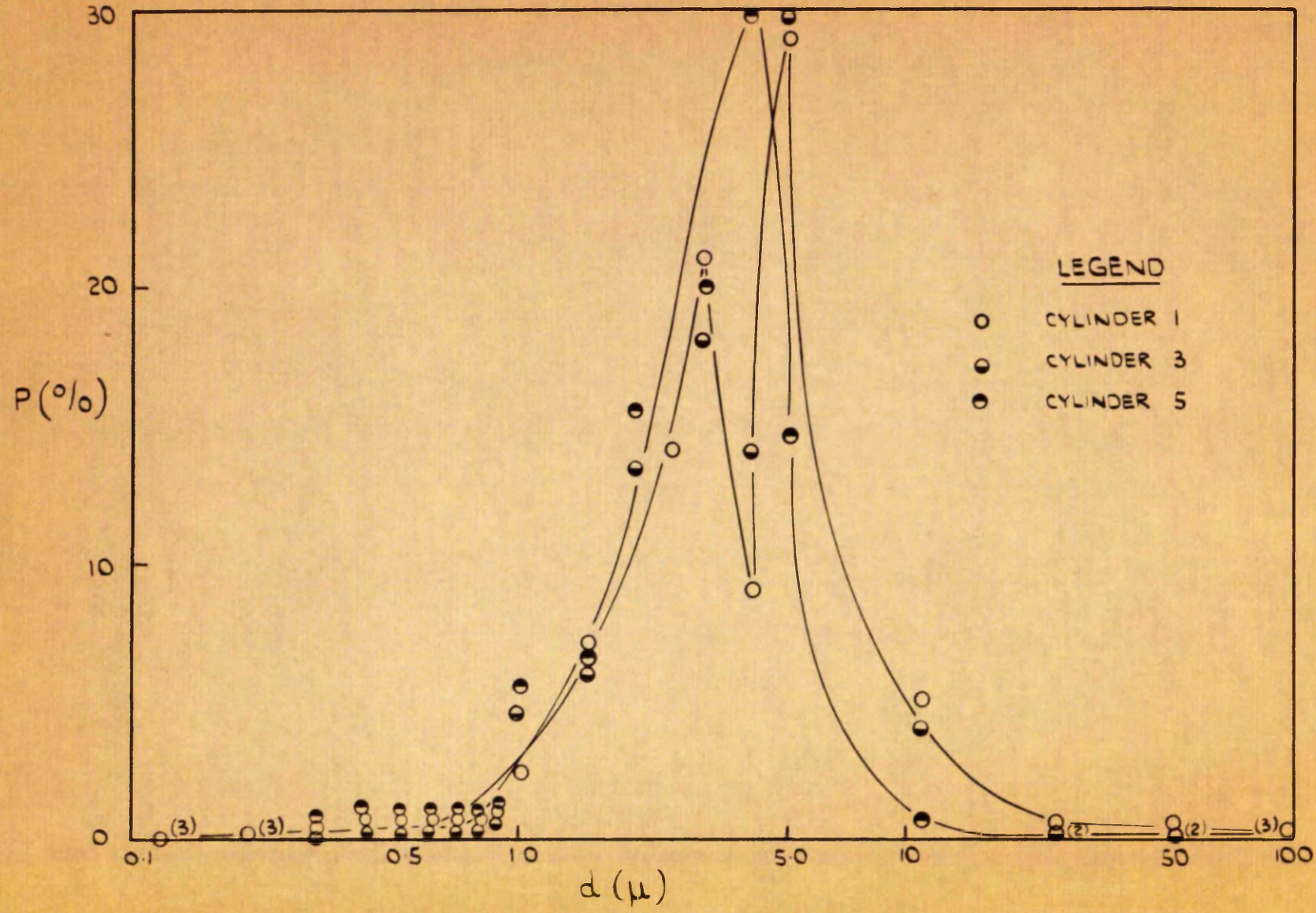

FIG 33 b.

PLOT OF B, % BULK VOLUME OCCUPIED,

vs d, PORE ENTRANCE DIAMETER (TEFLON)

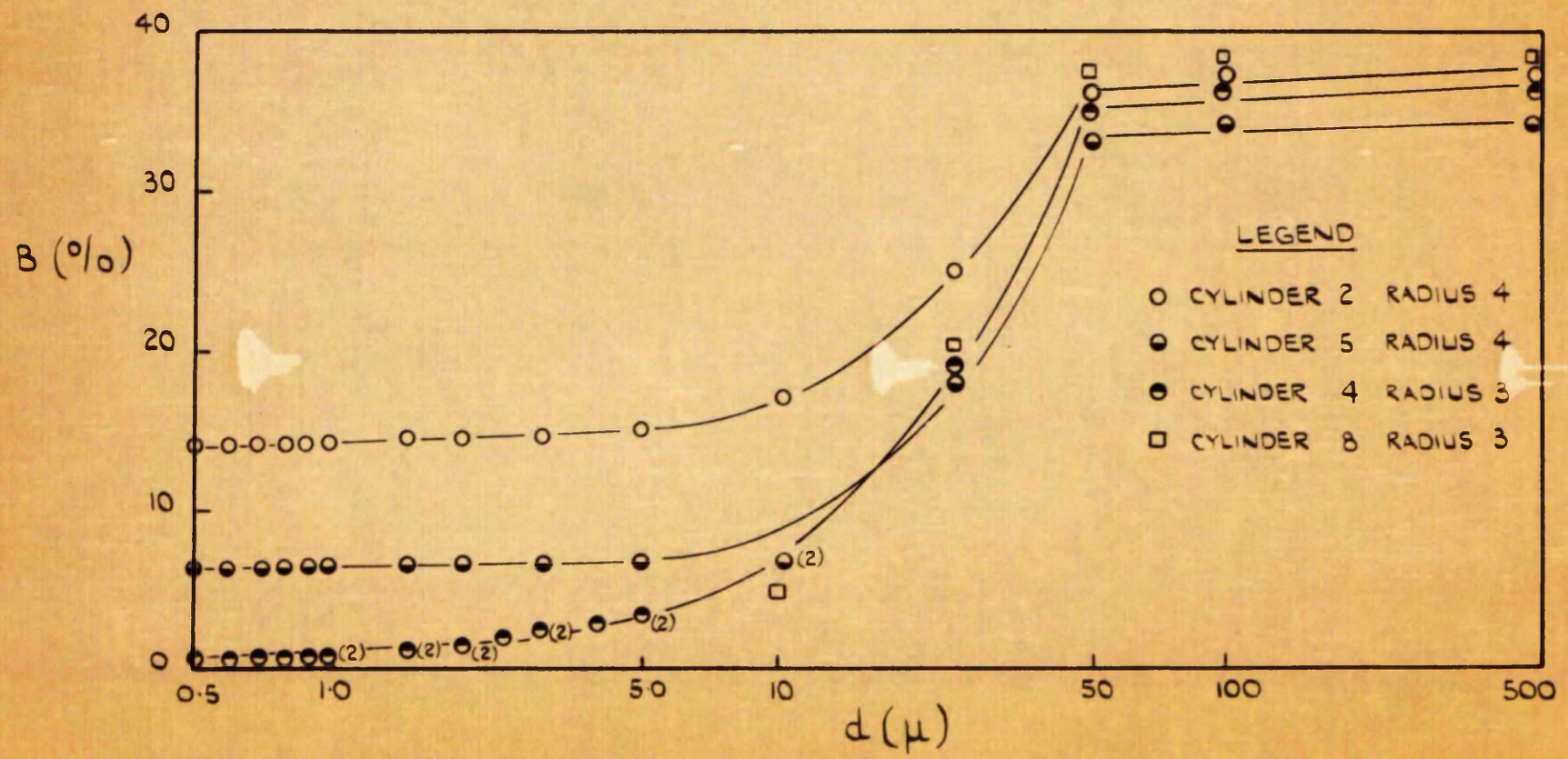

FIG.34d

PLOT OF P, % PORE VOLUME FILLED,

vs d, PORE ENTRANCE DIAMETER (TEFLON)

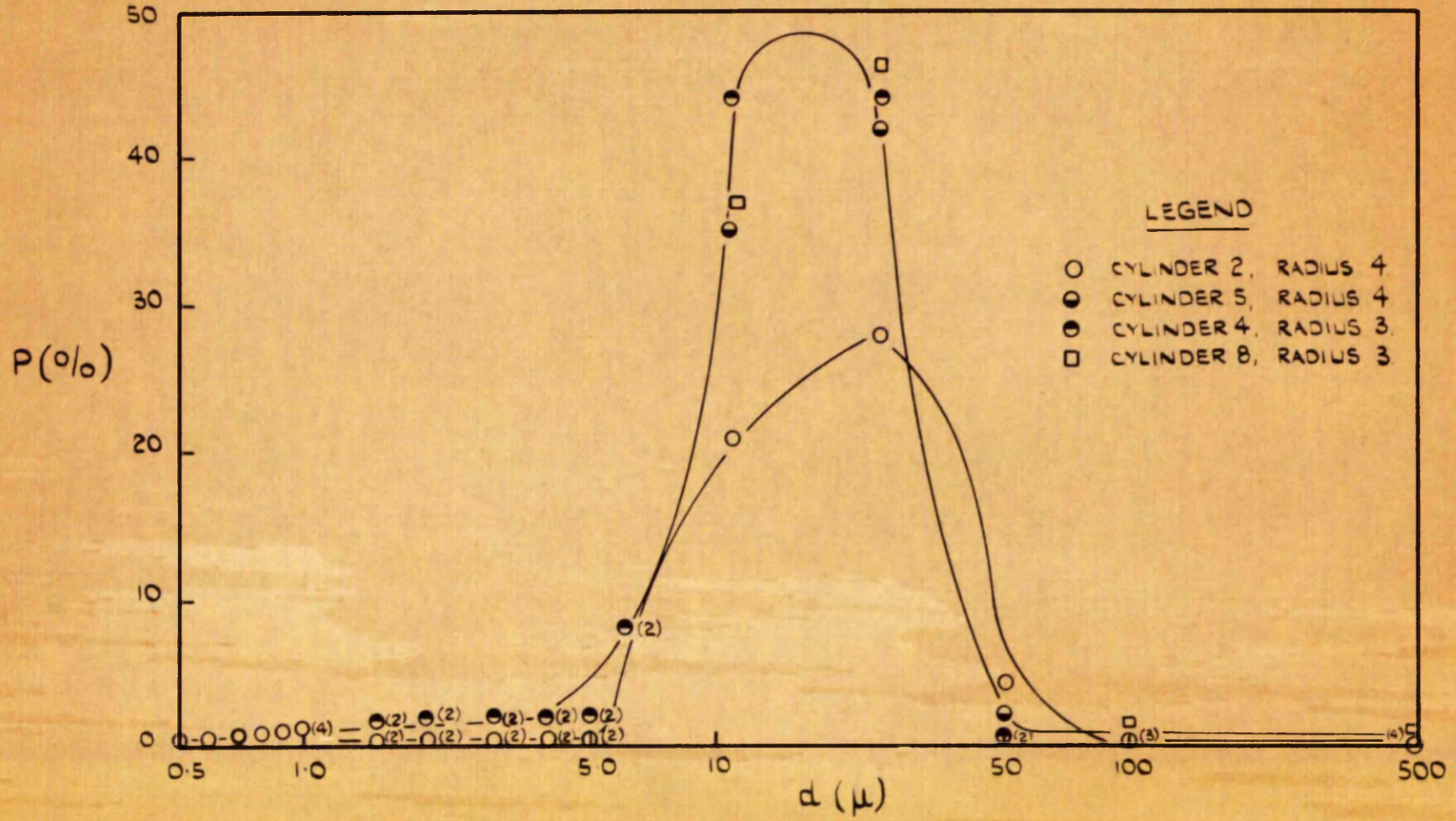

FIG. 34b

Table 9: Specimen Calculation of Pore Size Distribution Test

Date: August 14, 1964. Sample No. H125:6
Bulk Volume 4.28 c.c. Pore Volume 2.17 c.c. Sample Porosity 50.7%

Low Pressure Work

Time	Temp. (°C.)	Head (cm.Hg.)	Mercury Reading		Volume (cc.)	Corrected P.V. (cc.)	$\frac{P.V.}{B.V.}$ (%)	Porosity - $\frac{P.V.}{B.V.}$ (%)
			Initial (cc.)	Final (cc.)				
3.14	25.0	1.4	0.035	0.031	0.000	0.000	0.0	50.7
3.19	25.0	2.0	0.038	0.038	0.007	0.003	0.07	50.6
3.25	25.0	3.1	0.040	0.040	0.009	0.004	0.09	50.6
3.27	25.0	12.0	0.050	0.050	0.019	0.012	0.28	50.4
3.28	25.0	23.1	0.051	0.051	0.020	0.013	0.30	50.4
3.30	25.0	45.2	0.055	0.055	0.024	0.017	0.40	50.3
3.35	25.1	A+30.4	0.060	0.060	0.029	0.017	0.40	50.3

High Pressure Work

Time	lb./in.^{2} (gauge)	Ohm Reading		Accumulative		Corrected P.V. (cc.)	$\frac{P.V.}{B.V.}$ (%)	Porosity - $\frac{P.V.}{B.V.}$ (%)
		Initial (Ω)	Final (Ω)	ohms (Ω)	Volume (cc.)			
4.32	A	6.03	6.03	0	0	0.017	0.40	50.3
4.35	23	6.03	6.03	0	0	0.017	0.40	50.3
4.36	33	6.03	6.03	0	0	0.017	0.40	50.3
4.38	51	6.03	6.03	0	0	0.017	0.40	50.3
4.39	87	6.03	6.03	0	0	0.017	0.40	50.3
4.41	122	6.03	6.03	0	0	0.017	0.40	50.3
4.52	193	10.10	10.21	4.18	1.089	1.106	25.8	24.9
5.06	217	11.30	11.34	5.31	1.384	1.401	32.7	18.0
5.28	247	12.20	12.22	6.19	1.613	1.630	38.1	12.6
5.30	285	12.90	12.90	6.87	1.790	1.807	42.2	8.5
5.32	336	13.40	13.40	7.37	1.920	1.937	45.3	5.4
5.33	407	13.84	13.84	7.81	2.035	2.052	47.9	2.8
5.35	516	14.10	14.10	8.07	2.103	2.120	49.5	1.2
5.36	691	14.22	14.22	8.19	2.134	2.151	50.3	0.4
5.37	1047	14.28	14.28	8.25	2.150	2.167	50.6	0.1
5.40	1700	14.29	14.29	8.26	2.152	2.169	50.7	0.0

From the graphs of % pore volume and % bulk volume occupied against pore entrance diameter, the data in Table 10 was obtained.

Table 10: Characteristics of the Porous Media Obtained from Pore Size Distribution Curves

Material Grade	Mean Pore Diameter (μ)	% of Pore Volume Less than 1μ Diameter	% of Bulk Volume less than 1μ Diameter
H125	1.0	49.3	25
V5	4	6.7	3.0
CC2	0.45	97.8	38.5
Teflon r_4	20	38.4; 18.9	14.5; 6.5
r_3	20	2.8	1.0

The runs with Teflon cylinders of radius r_4 were not consistent and a mean value could not be taken. Hence there are two values for the percentage pore volume and bulk volume occupied by pores less than 1μ diameter.

APPENDIX 4

STATISTICAL ANALYSIS OF THE VALUES OF D FOR THE SERIES H125 - CARBON TETRACHLORIDE - METHANOL

Note: The values of D were calculated using the solution of the diffusion equation for short times.

Series of 18 Runs with Repeats

Legend

c_1	40 weight % CCl_4	r_1	0.77 cm, radius
c_2	50 weight % CCl_4	r_2	0.65 cm, radius
c_3	60 weight % CCl_4	r_3	0.52 cm, radius

a absorption d desorption

Individual Values of D

No. of Run	10^5 D (cm^2 sec^{-1})	10^5 D Repeat (cm^2 sec^{-1})
r_1 c_1 a	1.00	0.99
r_1 c_2 a	1.02	1.02
r_1 c_3 a	0.86	0.89
r_2 c_1 a	1.00	1.08
r_2 c_2 a	0.98	0.87
r_2 c_3 a	0.87	0.85
r_3 c_1 a	1.07	1.00
r_3 c_2 a	0.93	1.01
r_3 c_3 a	0.89	0.85
r_1 c_1 d	1.02	1.02
r_1 c_2 d	1.10	1.06
r_1 c_3 d	1.02	1.01

Cont'd/over

r_2 c_1 d	1.00	1.03
r_2 c_2 d	0.98	0.97
r_2 c_3 d	0.86	0.88
r_3 c_1 d	1.06	1.04
r_3 c_2 d	1.03	0.99
r_3 c_3 d	0.98	0.95

Sum over Repeats

	c_1			c_2			c_3			
	r_1	r_2	r_3	r_1	r_2	r_3	r_1	r_2	r_3	
a	1.99	2.08	2.07	2.04	1.85	1.94	1.75	1.72	1.74	17.18
d	2.04	2.03	2 10	2.16	1.96	2.02	2.03	1.74	1.93	18.00
										35.18

Sum over Radius

	c_1	c_2	c_3	
a	6.14	5.83	5.21	17.18
d	6.17	6.13	5.70	18.00
	12.31	11.96	10.91	35.18

Sum over Concentration

	r_1	r_2	r_3	
a	5.78	5.65	5.75	17.18
d	6.23	5.72	6.05	18.00
	12.01	11.37	11.80	35.18

Sum over Method

	r_1	r_2	r_3	
c_1	4.03	4.11	4.17	12.31
c_2	4.20	3.80	3.96	11.96
c_3	3.78	3.46	3.67	10.91
	12.01	11.37	11.80	35.18

Estimate of Variance of Effects and Interactions

$$\text{Correction Factor (CF)} = \frac{(\text{grand total})^2}{\text{total number of runs}}$$

$$\therefore \quad CF = \frac{(35.18)^2}{36} = 34.378677$$

concentration, c : $\dfrac{(12.31)^2 + (11.96)^2 + (10.91)^2}{12} - CF$

$= 0.088473$

radius, r : $\dfrac{(12.01)^2 + (11.37)^2 + (11.80)^2}{12} - CF$

$= 0.017739$

method, m : $\dfrac{(17.18)^2 + (18.00)^2}{18} - CF$

$= 0.018678$

interaction, cr : $\dfrac{(4.03)^2 \ldots + (3.96)^2 + (3.67)^2}{6} - CF - c - r$

$= 0.018211$

interaction, cm : $\dfrac{(6.14)^2 \ldots + (5.21)^2 + (5.70)^2}{6} - CF - c - m$

$= 0.008905$

interaction, rm : $\dfrac{(5.78)^2 \ldots + (5.75)^2 + (6.05)^2}{6} - CF - r - m$

$= 0.006106$

interaction, cmr : $\dfrac{(1.99)^2 + (2.04)^2 \ldots + (1.74)^2 + (1.93)^2}{2} - CF - c - m - r - cm - cr - rm$

$= 0.004211$

Residual = total - c - r - m - cr - cm - rm - cmr = 0.0194

Total = $(1.00)^2 + (1.02)^2 + \ldots + (0.99)^2 + (0.95)^2 - CF = 0.181723$

Statistical Table

Factor	No. of Degrees of Freedom	Sum of Squares	Mean Squares
concentration, c	2	0.088473	0.044236
radius, r	2	0.017739	0.008869
method, m	1	0.018678	0.018678
interaction, cr	4	0.018211	0.004552
interaction, cm	2	0.008905	0.004452
interaction, rm	2	0.066106	0.003053
interaction, cmr	4	0.004211	0.001052
residual	18	0.019400	0.001077
Total	35	0.181723	

The mean square of interaction or effect is compared with the mean square of the residual (also called the experimental variance). If, when the statistical tables are consulted, the interaction or effect is not significant, then a new residual is formed.

By inspection, interaction cmr is insignificant.

$\therefore$ New residual $= \dfrac{0.019400 + 0.004211}{18 + 4}$

$= 0.001073$ with 22 degrees of freedom (d of f)

the ratio of the mean squares is termed the F ratio.

<u>interaction rm</u> : $F = \dfrac{0.003053}{0.001073} = 2.85$ $\quad v_1 = 2$, $v_2 = 22$

where v_1 and v_2 are the number of degrees of freedom of the numerator and denominator respectively.

The table value is 3.44

$\therefore$ <u>rm</u> is insignificant at 5% level.

New residual $= \dfrac{0.023611 + 0.006106}{22 + 2}$

$= 0.001238$ with 24 d of f.

interaction cm: $F = \dfrac{0.004452}{0.001238} = 3.60$ $\quad v_1 = 2$, $v_2 = 24$

The table value $= 3.40$

$\therefore$ interaction cm is significant at 5% level

The residual is now fixed at 0.001238 with 24 d of f.

interaction cr : $F = \dfrac{0.004552}{0.001238} = 3.68$ $\quad v_1 = 4$, $v_2 = 24$

The table value $= 2.78$

$\therefore$ interaction cr is significant at 5% level

$\therefore$ $D = f_1 (cm) + f_2 (cr)$

APPENDIX 5

STATISTICAL ANALYSIS OF THE VALUES OF D^1 FOR THE SERIES H125 - CARBON TETRACHLORIDE - METHANOL

Table of Individual Values of D^1

No. of Run	$10^5 D^1$ (cm^2 $sec.^{-1}$)	$10^5 D^1$ Repeat (cm^2 $sec.^{-1}$)
r_1 c_1 a	1.95	1.94
r_1 c_2 a	1.99	2.00
r_1 c_3 a	1.68	1.74
r_2 c_1 a	1.92	2.09
r_2 c_2 a	1.88	1.68
r_2 c_3 a	1.67	1.64
r_3 c_1 a	2.06	1.91
r_3 c_2 a	1.79	1.93
r_3 c_3 a	1.71	1.62
r_1 c_1 d	1.99	2.00
r_1 c_2 d	2.14	2.07
r_1 c_3 d	1.99	1.98
r_2 c_1 d	1.92	1.99
r_2 c_2 d	1.88	1.88
r_2 c_3 d	1.65	1.70
r_3 c_1 d	2.04	1.98
r_3 c_2 d	1.98	1.89
r_3 c_3 d	1.89	1.81

Sum over repeats

	r_1	c_1 r_2	r_3	r_1	c_2 r_2	r_3	r_1	c_3 r_2	r_3	
a	3.89	4.01	3.97	3.99	3.56	3.72	3.42	3.31	3.33	33.20
d	3.99	3.91	4.02	4.21	3.76	3.87	3.97	3.35	3.70	34.78
										67.98

Sum over Radius

	c_1	c_2	c_3	
a	11.87	11.27	10.06	33.20
d	11.92	11.84	11.02	34.78
	23.79	23.11	21.08	67.98

Sum over concentration

	r_1	r_2	r_3	
a	11.30	10.88	11.02	33.20
d	12.17	11.02	11.59	34.78
	23.47	21.90	22.61	67.98

Sum over method

	c_1	c_2	c_3	
r_1	7.88	8.20	7.39	23.47
r_2	7.92	7.32	6.66	21.90
r_3	7.99	7.59	7.03	22.61
	23.79	23.11	21.08	67.98

Estimate of Variance of Effects and Interactions

Correction Factor (CF) $= \frac{(\text{grand total})^2}{\text{Total number of runs}} = \frac{(67.98)^2}{36} = 128.368900$

Concentration, c : $\frac{(23.79)^2 + (23.11)^2 + (21.08)^2}{12} - CF = 0.331316$

Radius, r : $\frac{(23.47)^2 + (21.90)^2 + (22.61)^2}{12} - CF = 0.103016$

Method, m : $\frac{(33.20)^2 + (34.78)^2}{18} - CF = 0.069344$

Interaction, cr: $\frac{(7.88)^2 + \cdots + (6.66)^2 + (7.03)^2}{4} - CF - c - r$

$= 0.066768$

Interaction, cm : $\frac{(11.87)^2 + \cdots + (10.06)^2 + (11.02)^2}{6} - CF - c - m$

$= 0.034740$

Interaction, rm : $\frac{(11.30)^2 + \cdots + (11.02)^2 + (11.59)^2}{6} - CF - r - m$

$= 0.022440$

Interaction, cmr : $\frac{(3.89)^2 + (3.99)^2 + \cdots + (3.33)^2 + (3.70)^2}{2} - CF - c - m - r - cr - cm - rm = 0.017076$

Residual: Total $- c - r - m - cr - cm - rm - cmr = 0.07720$

Total : $(1.95)^2 + (1.94)^2 + \cdots + (1.89)^2 + (1.81)^2 - CF = 0.721900$

Statistical Table

Factor	Degrees of Freedom	Sum of Squares	Mean Squares
concentration, c	2	0.331316	0.165658
radius, r	2	0.103016	0.051508
method, m	1	0.069344	0.069344
interaction, cr	4	0.066768	0.016692
interaction, cm	2	0.034740	0.017370
interaction, rm	2	0.022440	0.011220
interaction, cmr	4	0.017076	0.004269
residual	18	0.07720	0.004288
total	35	0.721900	

By inspection, interaction cmr is insignificant

$\therefore$ New residual $= \dfrac{0.017076 + 0.07720}{18 + 4}$

$= 0.004285$ with 22 d of F.

interaction rm: $F = \dfrac{0.01122}{0.004285} = 2.62$ $\quad v_1 = 2$, $v_2 = 22$

The table value is 3.44.

$\therefore$ Interaction rm is insignificant at 5% level.

$\therefore$ New residual $= \dfrac{22 \times 0.004285 + 0.022440}{22 + 2}$

$= 0.004862$ with 24 d of F.

Interaction cr: $F = \dfrac{0.016692}{0.004862} = 3.43$ $\quad v_1 = 4$, $v_2 = 24$

The table value is 2.78

$\therefore$ interaction cr is significant at 5% level

interaction cm : $F = \dfrac{0.01737}{0.004862} = 3.57$ $\quad v_1 = 2$, $v_2 = 24$

The table value is 3.40

$\therefore$ interaction cm is significant at the 5% level

$\therefore$ $D^1 = f_1 (cr) + f_2 (cm)$

B I B L I O G R A P H Y

(1) Akselrud, Russian Jour. Phys. Chem., 34, 132 (1960)

(2) Thiele, Ind. Eng. Chem., 31, 916 (1939).

(3) Aris, Chem. Eng. Science, 6, 267 (1956 - 57).

(4) Carberry, A.I.Ch. E., 8, 557 (1962).

(5) Crank and Henry, Trans. Far. Soc. 45, 1119 (1949).

(6) Arnold, J. Am. Chem. Soc. 52, 3937 (1930).

(7) Frenkel, Kinetic Theory of Liquids, pp. 93, 174, 188 (1946).

(8) Einstein, Ann. Phys. 17., 549 (1905).

(9) Sutherland, Phil. Mag., 3, 784 (1905).

(10) MacDonald, Ph.D. thesis, Glasgow University, (1957).

(11) Kamal and Canjar, A.I.Ch.E. Journ., 8, 329 (1962).

(12) Kirkwood, J. Chem. Phys., 14. 180 and 347 (1946).

(13) Darken, Trans. Am. Inst. Mining Eng., (Metal Division) 175, 184, (1948).

(14) Bearman, Jour. Phys. Chem., 65, 1961 (1961).

(15) Laity, Jour. Phys. Chem., 63, 80 (1959).

(16) Horrocks and McLaughlin, Trans. Far. Soc., 58, 1357 (1962).

(17) Tyrrell, Diffusion and Heat Flow in Liquids, p.142.

(18) Hall, Wishaw and Stokes, Jour. Am. Chem. Soc. 75, 1556 (1953).

(19) Eyring, Theory of Rate Processes; Jour. Chem. Phys. 6, 896 (1937); Chem. Rev., 28, 301, (1941); Jour. Phys. Chem., 44, 981 (1940); Ind. Eng. Chem., 33, 430 (1941)

(20) Proceedings of the International Conference on Crystal Growth, p.301, (1958).

(21) Olander, A. I. Ch. E., 9, 207 (1963).

(22) Wilke, C.E.P., 45, 218 (1949).

(23) Prager, Jour. Chem. Phys., 33, 122 (1960).

(24) Goodknight, Klikoff and Fatt, Jour. Phys. Chem., 64, 1162 (1960).

(25) ibid, 65, 1709 (1961).

(26) Barrer, Jour. Phys. Chem., 57, 35 (1953).

(27) Erdos and Jiro, Coll Czech. Chem. Comm., 22, 862 (1957).

(28) Petersen, A.I.Ch.E., 4, 343 (1958).

(29) De La Rue and Tobias, Conductivities of Random Dispersions, presented at the 107th meeting of the electro chemical society, Cincinnati, (1955).

(30) Hoogschagen, Ind. Eng. Chem., 47, 906 (1955).

(31) Okromchedlidtse, Soobsheh, Akad. Nauk, Gruz. S.S.S.R., 28 535 (1962).

(32) Bird, Advances in Chemical Engineering, Vol. 1., pp. 155 et seq.

(33) Clarke, Jour. Chem. Phys., 27, 29 (1957).

(34) English and Dole, J. Am. Chem. Soc., 72, 3261, (1950).

(35) Gosting and Morris, J. Am. Chem. Soc., 71, 1998 (1949).

(36) Tsang, Jour. Appl. Phys., 32, 1518, (1961).

(37) Helfferich, Jour. Chem. Phys., 38, 1688 (1963).

(38) Crank, The Mathematics of Diffusion, p.64 (1956).

(39) Internal Instruction Pamphlet, Building Research Station, Garston, Herts.

(40) Vogel, Quantitiative Inorganic Analysis, 2nd Edition, p.251.

(41) International Critical Tables, Vol. II, p.336.

(42) Timmermans, Vol. 4., p.313.

(43) Little and MacDonald, unpublished work, Department of Chemical Technology, Royal College of Science and Technology, Glasgow.

(44) Stewart, Ph.D. Thesis, Glasgow University (1960).

(45) Cady and Williams, Jour. Phys. Chem., 39, 87 (1935).

(46) Friedman and Kraemer, J. Am. Chem. Soc., 52, 1295 (1930).

(47) Stokes, J. Am. Chem. Soc., 72, 763 and 2243 (1950).

(48) Calvet, J. Chim. Phys. 44, 47 (1947).

(49) Tsvetkov, J.E.T.F., 21, 701 (1951).

(50) Hammond and Stokes, Trans. Far. Soc., 51, 1641 (1955).

(51) Robinson and Stokes, Electrolyte Solutions.

(52) Lange, Handbook of Chemistry, ninth edition, Pauling, J. Am. Chem. Soc., 49, 765 (1927).

(53) Timmermans, Physico-Chemical Properties of Binary Solutions, 3, 486.

(54) ibid., 3, 363.

(55) ibid., 2, 279.